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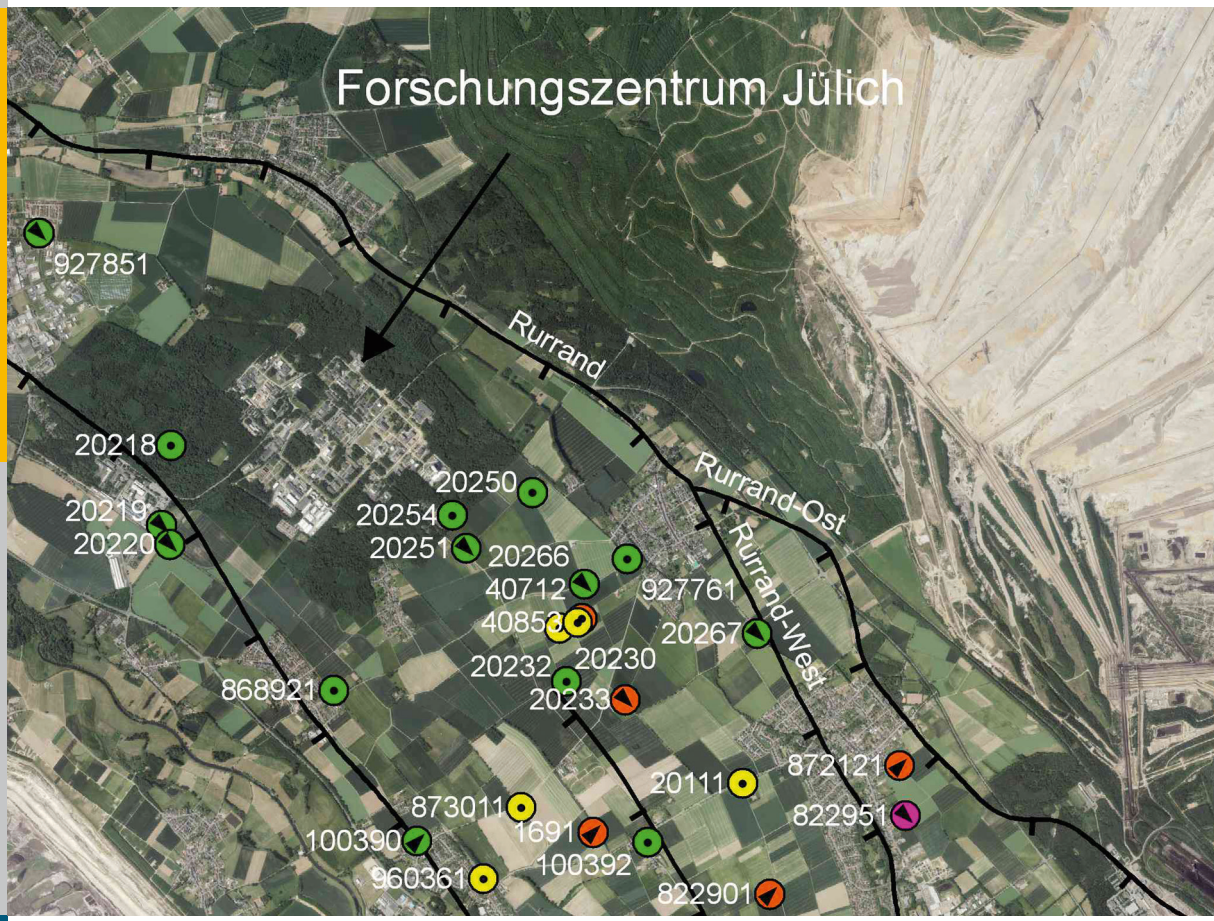
David Stefan Vonberg



Energie & Umwelt / Energy & Environment
Band / Volume 293
ISBN 978-3-95806-099-9

JÜLICH FORSCHUNGSZENTRUM

Schriften des Forschungszentrums Jülich
Reihe Energie & Umwelt / Energy & Environment Band / Volume 293

Forschungszentrum Jülich GmbH
Institute of Bio- and Geosciences
Agrosphere (IBG-3)

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ISSN 1866-1793 ISBN 978-3-95806-099-9

Bibliographic information published by the Deutsche Nationalbibliothek.
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Publisher and Distributor: Forschungszentrum Jülich GmbH
Zentralbibliothek
52425 Jülich
Tel: +49 2461 61-5368
Fax: +49 2461 61-6103
Email: zb-publikation@fz-juelich.de
www.fz-juelich.de/zb

Cover Design: Grafische Medien, Forschungszentrum Jülich GmbH

Printer: Grafische Medien, Forschungszentrum Jülich GmbH

Schriften des Forschungszentrums Jülich
Reihe Energie & Umwelt / Energy & Environment, Band / Volume 293

D 82 (Diss. RWTH Aachen University, 2015)

ISSN 1866-1793
ISBN 978-3-95806-099-9

The complete volume is freely available on the Internet on the Jülicher Open Access Server (JuSER) at www.fz-juelich.de/zb/openaccess.

Summary

Atrazine, one of the worldwide most widespread herbicides, was banned in Germany in 1991 and in the European Union in 2004, due to findings of atrazine concentrations in ground- and drinking waters exceeding the threshold value of 0.1 µg L^{-1}. Nevertheless atrazine and the metabolite deethylatrazine were still detected in German aquifers more than 10 years after its prohibition, often without any considerable decreasing trend in groundwater concentration. Because atrazine was already found to be persistent in soils for more than two decades after the last application, the hypothesis was raised that a continued release of atrazine residues from the soil into groundwaters might sustain atrazine groundwater concentrations on elevated levels.

The overall objective of this study was to investigate the occurrence and concentration trends of atrazine and its main metabolites in the groundwater-soil environment after the prohibition of its use. Accordingly, in this study results of i) 20 years of atrazine groundwater monitoring of a a shallow aquifer in western Germany since its ban and ii) atrazine soil residue analyses in the vadose zone of the same study area 21 years after its ban are presented.

The phreatic Zwischenscholle aquifer located in the Lower Rhine Embayment is exposed to intensive agricultural land use and is highly susceptible to contaminants due to a shallow water table. In total 60 observation wells (OWs) have been monitored since 1991, of which 11 are sampled monthly today. Descriptive statistics of monitoring data were derived using the “regression on order statistics” (ROS) data censoring approach, estimating values for nonquantifiable values rather than substitute them by e.g. half of the limit of quantification and taking the risk of biasing statistical parameters. The monitoring data shows that even 20 years after the ban of atrazine, the groundwater concentrations of sampled OWs remain on a level close to the threshold value of 0.1 µg L^{-1} without any considerable decrease. The spatial distribution of atrazine concentrations is highly heterogeneous with OWs exhibiting permanently concentrations above the regulatory threshold on the one hand and other OWs

with concentrations mostly below the limit of quantification (LOQ) on the other hand. Here atrazine concentrations show upward, downward or approximately constant trends. The deethylatrazine-to-atrazine ratio (DAR) was used to distinguish between diffuse – and point-source contaminations. A DAR around unity (slightly smaller for thin vadose zones like for the investigated aquifer) suggests a contamination of an aquifer by diffuse pathways, resulting in significant metabolization of atrazine to deethylatrazine due to a longer contact time to soil microorganisms. Conversely, point-source contaminations where the contaminant enters the aquifer directly by e.g. macropore flow results in negligible deethylation and hence a DAR close to zero. A global mean DAR value of 0.84 for the monitoring data of the Zwischenscholle aquifer indicates mainly diffuse contamination. Also most of the DARs for single observation wells suggest mainly diffuse pollution, except for one OW with a mean DAR of 0.02, clearly indicating point-source contamination. Principle Component Analysis (PCA) of the monitoring dataset demonstrated relationships between the metabolite deisopropylatrazine and its parent compound simazine but not with atrazine, and deethylatrazine, atrazine, nitrate, and the specific electrical conductivity. These parameters indicate diffuse agricultural impacts on groundwater quality.

The groundwater monitoring findings point at the difficulty to estimate mean concentrations of contamination for entire aquifers and to evaluate groundwater quality based on average parameters. However, analytical data of monthly sampled single observation wells provide adequate information to characterize local contamination and evolutionary trends of pollutant concentration.

For atrazine soil residue analysis three soil cores reaching down to the groundwater table (approximately 3 m below soil surface) were taken in an agricultural field where atrazine was applied prior to its ban. It is uncertain if atrazine was applied in total two or three times with a recommended dose of 0.96 kg ha^{-1}. Eight layers were separated (0-10 cm, 10-30 cm, 30-60 cm, 60-100 cm, 100-150 cm, 150-200 cm, 200-250 cm, 250-300 cm) for atrazine residue analysis and soil parameters (grain size distribution, pH, cation exchange capacity (CEC_{eff}) and organic carbon content). Soil samples of each layer were extracted using accelerated

solvent extraction (ASE) and analyzed by LC-MS/MS analysis. Prior to this analysis, a method validation was conducted to find optimum extraction parameter combinations. For all extractions a methanol/water (4:1, v/v) solvent was used. The highest quantifiable atrazine extraction yield amongst all extraction parameter combinations between 100°C and 135°C and 100 bar, 150 bar and 207 bar was obtained for 100°C and 207 bar. Atrazine yields were generally higher for higher pressures. Possibly the higher pressure facilitates soil matrix penetration by the solvent. Extractions using 135°C and the highest pressure of 207 bar resulted in quantified concentration of atrazine 31 % lower than those using 100°C. Probably, the higher extraction temperature lead to an increased co-extraction of soil-matrix compounds, which caused a quenching effect and hence less quantifiable atrazine.

Extracted atrazine concentrations of the different layers of the soil cores ranged between 0.2 $\mu g\ kg^{-1}$ and 0.01 $\mu g\ kg^{-1}$ for topsoil and subsoil, respectively. Averaged residual atrazine accounts for 0.01 % of the applied mass in the top layer and 0.07 % in the total soil profile (for in total 3 applications). However, the calculation can only be treated as a conservative estimate, because spatial information of atrazine field applications and the correct number of applications (2 or 3 times) are not available. A complete and instantaneous remobilization of atrazine residues from the unsaturated zone, leaching to and mixing with the entire groundwater body would result in a mean groundwater concentration of 0.002 $\mu g\ L^{-1}$. In contrast, considering local atrazine groundwater contamination below an atrazine residue area by a complete instantaneous remobilization of the latter and vertical mixing with the groundwater body below, atrazine groundwater concentrations would be 0.068 $\mu g\ L^{-1}$. Based on the first scenario, long term leaching of aged atrazine residues from the vadose zone seems to marginally contribute to sustaining average groundwater concentrations of the Zwischenscholle aquifer, which remained constantly close to the threshold limit of 0.1 $\mu g\ L^{-1}$ even 20 years after the ban of atrazine. In contrast, the second scenario shows that ongoing local leaching of atrazine from soil residues might result in locally elevated atrazine groundwater concentrations, what might be reflected by the high spatial variability in atrazine groundwater concentrations in the investigated aquifer. A conservative estimate suggests an

atrazine half-life value of approximately 2 years for the soil zone, which is significantly higher than the highest atrazine half-life values found in literature (433 days [1.19 years] for top soil). This value only can be taken as rough orientation and most probably underestimates the atrazine half-life time in this soil, because i) non-extractable atrazine could not be included in the calculation and ii) the first two applications were executed before 1991 (information of the exact time of application is missing) and iii) for aged atrazine residues and increased resistance to biodegradation, atrazine degradation in soils rather follows multi-rate kinetics than assumed first order kinetics, what could result in an overestimation of decay rates. These findings show that atrazine persistence in the field might be distinctively higher than predicted assuming first-order degradation kinetics and using half-life values obtained from lab experiments which reach a maximum of 433 days for topsoils. Generally, literature values for the organic carbon normalized distribution coefficient (K_{OC}) and dissipation half-life value for atrazine show a wide range between 25 and 600 L Kg^{-1} and a few days up to 433 days. Until now there is a lack of the understanding of how herbicide degradation rates vary according to spatial heterogeneity of soil properties. Furthermore, important determining factors influencing degradation like microbial ecology and its spatial variability have been neglected so far for pesticide fate predictions. Accordingly, the accuracy of model predictions of catchment scale atrazine behavior on the long-term based on first-order-kinetics and standard laboratory-derived sorption parameter values may be not reliable. Thus the risk of long-term adverse environmental effects may be higher than estimated. In consequence, there is a need for more realistic pesticide risk assessments and regulation procedures besides standard models for pesticide fate predictions. Finally, considering the key finding that the persistence of particular pesticides in groundwater may be highly underestimated by pesticide fate predictions based on laboratory short-term studies, contaminant monitoring in the groundwater-soil environment remains of highest importance, to i) detect potential groundwater contaminations, ii) re-consider pesticide fate predictions, iii) limit or ban the use of contaminants frequently exceeding thresholds and iv) treat drinking water adequately.

Zusammenfassung

Atrazin, eines der am häufigsten verwendeten Herbizide weltweit, wurde aufgrund von häufigen Überschreitungen des Grenzwerts für Grund- und Trinkwasser (0.1 µg L^{-1}) in Deutschland im Jahr 1991 und in der gesamten Europäischen Union im Jahr 2004 verboten. Nichtsdestotrotz wurden Atrazin und sein Metabolit Desethylatrazin in deutschen Grundwässern noch mehr als 10 Jahre nach dessen Verbot detektiert, oftmals ohne Konzentrationsabnahme. Aufgrund der Tatsache, dass Atrazin-Rückstände in Böden in vorigen Studien als äußerst persistent bewertet wurden, wurde die Hypothese aufgestellt, dass eine fortwährende Freisetzung von Atrazin von der Bodenmatrix mit anschließender Versickerung eine Gefahr für die Grundwasserqualität darstellen könnte.

Das Hauptanliegen dieser Studie war die Analyse von Konzentrationen von Atrazin, dessen Hauptmetaboliten und Trends sowie die Verbreitung in den Kompartimenten Grundwasser und Boden zwei Jahrzehnte nach dessen Verbot. Demnach präsentiert diese Studie Ergebnisse i) des 20 Jahre andauernden Grundwasser-Monitorings von Atrazin und anderen Parametern des Zwischenschollen Aquifers, der in der niederrheinischen Bucht gelegen ist und ii) der Analyse von Atrazin-Rückständen in der Bodenzone desselben Untersuchungsgebiets 21 Jahre nach dessen Verbot.

Der phreatische Aquifer gilt aufgrund von oberflächennahem Grundwasser für Kontaminationen von Umweltchemikalien als gefährdet und ist zudem intensiver Landwirtschaft ausgesetzt. Das Monitoring-System besteht aus insgesamt 60 Grundwassermessstellen (GWM) seit 1991, von denen heute 15 monatlich beprobt werden. Die statistische Darstellung der Monitoring-Daten wurde mit Hilfe der „regression on order statistics“ Methode (ROS) ermöglicht, bei der die Werte der Datenfraktion, die aus nicht bestimmbaren Werten besteht, geschätzt werden und nicht – wie oft üblich und häufig verfälschend – mit z.B. der Hälfte der Bestimmungsgrenze substituiert werden. Die statistische Auswertung aller beprobten GWMs hat gezeigt, dass 20 Jahre nach dem Verbot Atrazin-Grundwasserkonzentrationen ohne erkennbare Abnahme auf einem Niveau nahe

des Grenzwertes (0.1 µg L^{-1}) verbleiben. Die räumliche Verteilung der Atrazin Konzentrationen ist äußerst heterogen, einerseits mit GWMs, bei denen Konzentrationen permanent oberhalb des Grenzwertes liegen, und andererseits GWMs, bei denen Atrazin Konzentrationen stets nicht quantifizierbar sind bzw. unterhalb der Quantifizierungsgrenze (LOQ) liegen (eine Unterscheidung zwischen Nachweis- und Quantifizierungsgrenze der bestimmten Parameter wurde von dem externen Labor nicht angegeben und stets als < LOQ deklariert). Hierbei zeigen die Zeitreihen der Atrazin-Konzentrationen entweder Aufwärts-, Abwärts- oder annäherungsweise konstante Trends. Das Verhältnis von Desethylatrazin zu Atrazin (DAR) wurde als Indikator zur Unterscheidung von diffusen Einträgen und Punktquellen genutzt. DAR-Werte um 1 (geringfügig kleiner bei geringmächtigen vadosen Zonen) legen diffuse Quellen der Grundwasserverunreinigungen nahe, bei denen es zu einer signifikanten Metabolisierung von Atrazin zu Desethylatrazin durch längere Kontaktzeiten zu Bodenmikroorganismen kommt. Dem entgegen ist bei Punktquellen, bei denen die Substanz den Aquifer direkt über z.B. Makroporenfluss erreicht, die Transformation von Atrazin vernachlässigbar klein und führt demnach zu einem DAR-Wert nahe null. Ein globales DAR Mittel von 0.84 für den untersuchten Aquifer spricht überwiegend für diffuse Einträge von Atrazin ins Grundwasser. Eine Betrachtung der DAR-Werte für einzelne Grundwassermessstellen zeigt mit Ausnahme von einem Wert von 0.02, der eindeutig auf eine Punktquelle verweist, auch hauptsächlich diffuse Einträge an. Eine Hauptkomponenten-Analyse (PCA) des Monitoring-Datensatzes legte Korrelationen zwischen dem Metaboliten Desisopropylatrazin und der neben Atrazin möglichen Ausgangssubstanz Simazin, nicht jedoch Atrazin, offen. Weitere Korrelationen zwischen Desethylatrazin, Atrazin, Nitrat und der spezifischen elektrischen Leitfähigkeit konnten identifiziert werden, Parameter, die allesamt diffuse landwirtschaftliche Einträge in das Grundwasser anzeigen.

Zusammenfassend deuten die Monitoring-Ergebnisse darauf hin, dass die Schätzung von mittleren Konzentrationen von Kontaminationen für gesamte Grundwasserkörper und die auf gemittelten Parametern basierende Beurteilung der Grundwasserqualität problematisch ist.

Im Gegensatz dazu können Punktdaten der jeweiligen GWMs ausreichende Informationen liefern, um lokale Kontaminationen und Konzentrations-Trends zu charakterisieren.

Für die Analyse der Atrazin-Rückstände in der Bodenzone wurden drei Bohrkerne bis zur Grundwasseroberfläche (ca. 3 m unterhalb der Geländeoberkante) auf landwirtschaftlichem Nutzgrund mit Atrazin-Applikationsgeschichte genommen. Es ist unbekannt, ob Atrazin insgesamt zwei oder dreimal mit der empfohlenen Dosis von 0.96 kg ha^{-1} appliziert wurde. Acht Schichten (0-10 cm, 10-30 cm, 30-60 cm, 60-100 cm, 100-150 cm, 150-200 cm, 200-250 cm, 250-300 cm) wurden für die Untersuchung auf Atrazin-Rückstände getrennt, mit der „accelerated solvent extraction“ (ASE) Methode extrahiert und mittels Flüssigchromatographie mit Massenspektometrie/Massenspektrometrie-Kopplung (LC-MS/MS) quantifiziert. Vor jener Analyse wurde eine Methodenvalidierung durchgeführt, um die optimalen Extraktionsparameter zu bestimmen. Für alle Extraktionen wurde ein Lösungsmittelgemisch von Methanol/Wasser (4:1, v/v) benutzt. Die höchste Atrazin-Ausbeute wurde mit den Extraktionsparametern 100°C und 207 bar unter allen Parameterkombinationen zwischen 100°C, 135°C, und 100 bar, 150 bar und 207 bar erzielt. Generell nahm die Ausbeute mit steigendem Druck zu, durch die wahrscheinlich die Durchdringung der Bodenmatrix mit dem Lösungsmittel verstärkt wurde. Extraktionen mit 135°C und 206.8 bar führten zu Atrazin-Konzentrationen, die 31% geringer waren als die bei 100°C. Hierbei führte die erhöhte Temperatur zu einer verstärkten Ko-Extraktion von Bodenmatrix-Bestandteilen, welche einen Quenching-Effekt verursachten, verbunden mit weniger quantifizierbarem Atrazin.

Extrahierte Atrazin-Konzentrationen reichten von 0.2 $\mu g\ kg^{-1}$ (Oberboden) bis 0.01 $\mu g\ kg^{-1}$ (Unterboden). Quantifizierbare Atrazin-Rückstände betragen im Mittel für den Oberboden und für das komplette Bodenprofil 0.01 % und 0.07 % der gesamten Applikationsmenge (für 3 Applikationen). Dennoch darf diese Berechnung nur als vorsichtige Schätzung angesehen werden, da genauere Informationen über räumliche Atrazin-Konzentrationsverteilungen und die genaue Anzahl an Atrazin-Applikationen (2 oder 3) nicht bekannt ist. Eine vollständige, sofortige Auswaschung aller Atrazin-Rückstände der ungesättigten Zone und Mischung mit

dem Grundwasser würde in einer mittleren Atrazin-Konzentration von 0.002 µg L^{-1} resultieren. Im Gegensatz dazu würde eine lokale Grundwasserkontamination unterhalb einer Fläche mit oben quantifizierten Atrazin-Residuen bei vollständiger und sofortiger Auswaschung eine Konzentration von 0.068 µg L^{-1} aufweisen. Das erste Szenario zeigt, dass Langzeit-Auswaschung von gealterten Atrazin-Rückständen aus der vadosen Zone nur geringfügig dazu beiträgt, dass mittlere Atrazin-Konzentrationen des untersuchten Aquifers noch 20 Jahre nach dessen Verbot auf einem relativ konstanten Niveau nahe des Grenzwerts von 0.1 µg L^{-1} verbleiben. Im Gegensatz dazu zeigt das zweite Szenario, dass Remobilisierung und Transport von Atrazin aus der Bodenzone lokal zu höheren Atrazin-Konzentrationen im Grundwasser beitragen können, was sich möglicherweise auch in der ausgeprägten räumlichen Heterogenität der Atrazin-Grundwasserkonzentrationen des Zwischenschollen Aquifers widerspiegelt.

Eine vorsichtige Schätzung beziffert die Atrazin-Halbwertszeit innerhalb der Bodenzone auf annäherungsweise zwei Jahre, was bedeutend höher ist als die höchsten Werte aus der Literatur (433 Tage [1.19 Jahre] für Oberboden). Auch hier kann dieser Wert nur als grobe Orientierung gesehen werden, unterschätzt aber wahrscheinlich noch die Atrazin Halbwertszeit in diesem Boden, weil i) nicht-extrahierbares Atrazin nicht in die Berechnung mit einbezogen werden konnte, ii) die zwei ersten Applikation vor dem Jahr 1991 stattfanden (genaue Zeitangaben für Applikationen konnten nicht ermittelt werden) und iii) die Degradation gealterter Atrazin-Rückstände und damit verbundene erhöhte Resistenz gegenüber Biodegradation eher durch Multi-Raten Kinetik anstelle der Berechnung zugrunde liegenden Kinetik erster Ordnung charakterisiert wird, mit der Folge, dass Abbau-Raten überschätzt werden könnten. Diese Erkenntnisse deuten darauf hin, dass die Atrazin-Persistenz im Feld deutlich höher ist, als es Vorhersagen basierend auf Abbau-Kinetik erster Ordnung und Atrazin-Halbwertszeiten, die im Labor ermittelt wurden und Werte bis 433 Tage für Oberböden erreichen, nahelegen.

Im Allgemeinen variieren Literaturwerte sehr stark, sowohl für den auf den organischen Kohlenstoff normierten Sorptionskoeffizienten (K_{OC}) mit Werten zwischen 25 und 600 L kg-1,

als auch für die Halbwertszeit mit Werten zwischen wenigen Tagen und 433 Tagen. Bis heute ist kaum bekannt, wie die Abbau-Raten für Herbizide in Bezug auf die räumliche Heterogenität von Bodeneigenschaften variieren. Zudem wurden wichtige Faktoren, die das Abbauverhalten von Pestiziden in Böden maßgeblich bestimmen, wie die der mikrobiellen Ökologie und ihre räumliche Variabilität bei Modell-Simulationen nicht näher einbezogen. Demnach ist die Relevanz von Modell-Vorhersagen für das Langzeit-Verhalten von Atrazin auf der Skala von Einzugsgebieten sehr fragwürdig. Außerdem können die toxischen Wirkungen von Atrazin möglicherweise stärker ausfallen, als geschätzt. Aufgrund dieser Tatsache wird deutlich, dass eine große Notwendigkeit für realistischere Gefährdungsabschätzungen und Überarbeitung von Standardverfahren für die Zulassung von Pestiziden besteht. In Anbetracht der Erkenntnis, dass die Persistenz bestimmter Pestizide im Grundwasser stark von Modellvorhersagen basierend auf Kurzzeit-Laborstudien unterschätzt werden kann, bleibt das Monitoring von Umwelttoxinen im Grundwasser und Boden essentiell, um i) mögliche Grundwasserkontaminationen zu erkennen, ii) Vorhersagen über das Abbauverhalten zu überdenken, iii) den Einsatz von Agrarchemikalien, die Grenzwerte ständig überschreiten, einzudämmen oder ganz zu verbieten und iv) Trinkwasser angemessen aufzubereiten.

Danksagung

Ich möchte mich zunächst bei Allen herzlich bedanken, die mir die Möglichkeit eröffnet haben, im Institut für Bio- und Geowissenschaften 3 (IBG-3): Agrosphäre, Forschungszentrum Jülich GmbH, zu promovieren und mich dabei unterstützt haben. Dazu gehören in erster Linie meine Betreuer in Jülich Prof. Dr. Jan Vanderborght, PD Dr. Peter Burauel, mein Doktorvater Prof. Dr. Thomas Rüde vom Lehr- und Forschungsgebiet Hydrogeologie der RWTH Aachen und Prof. Dr. Harry Vereecken, Institutsleiter des IBG 3, dem ich für meine Einstellung in der Agrosphäre danken möchte. Besonderer Dank gilt dem Erftverband, stellvertretend durch unseren Hauptansprechpartner Herrn Dr. Nils Cremer, der verschiedene Daten zur hydrogeologischen Beschaffenheit der Jülicher Zwischenscholle und der Analytik von Grundwasserproben zur Verfügung gestellt hat und darüber hinaus bei Fragen zur Grundwasserbeschaffenheit der Zwischenscholle mit seiner Fachkompetenz zur Seite stand und die Arbeit bereichert hat.

Für die Hilfe bei der Optimierung der Atrazin-Analytik möchte ich mich bei Frau Dr. Diana Hofmann bedanken. Stephan Köppchen, der die LC-MS/MS Analytik durchgeführt hat und darüber hinaus seine Expertise in die Methodenentwicklung der Atrazin-Analytik mit eingebracht hat, danke ich herzlich für sein Engagement und seine Freundschaft. Thomas Pütz möchte ich für die Kommunikation zwischen unserem Team der Agrosphäre und den Landwirten der Jülicher Zwischenscholle, dem Erftverband und der Landwirtschaftskammer, sowie für die Versorgung mit Datensätzen, die für diese Arbeit essentiell waren, danken. In diesem Zusammenhang sind die Bauern Wilhelm Milz und Willi Baumann zu erwähnen, für deren Kooperation und Erlaubnis für die Bodenprobenahme auf ihren landwirtschaftlichen Flächen ich meine Dankbarkeit zum Ausdruck bringen möchte. Michael Herbst stand mir stets bei Statistik-Fragen und durch die Bereitstellung verschiedenster Daten der Jülicher Zwischenscholle mit seiner Expertise zur Seite, wofür ich ihm meinen Dank ausspreche. Für die Hilfe bei den Bodenprobenahmen durch Steuerung des Bohrgeräts danke ich Rainer Harms.

Für die engagierte Hilfe bei der Laborarbeit möchte ich mich bei der Bachelor-Studentin Anna Lelickens sowie der Auszubildenden Julia Hamacher herzlich bedanken.

Auch Personen wie Willi Benders, die seit Jahren die verschiedenen Grundwassermessstellen der Jülicher Zwischenscholle monatlich beproben und somit die Grundlage für meine Arbeit geschaffen haben, möchte ich meine große Wertschätzung zum Ausdruck bringen. Des Weiteren sind für die Analytik des totalen Kohlenstoffgehalts (TOC) und der Kationenaustauschkapazität (CEC) von Bodenproben Frau Bachhausen und Frau Lippert vom Zentralinstitut für Engineering, Elektronik und Analytik (ZEA-3) des Forschungszentrums Jülich zu danken.

Abseits des Arbeitsumfeldes möchte ich ganz besonderen Dank meiner Familie und meiner Frau Graciele aussprechen, die mich immer unterstützt haben und so im Hintergrund maßgeblich am Gelingen der Arbeit beteiligt waren.

Preface

This dissertation is based on the one hand on two scientific peer-reviewed articles, of which one is titled “20 years of long-term atrazine monitoring in a shallow aquifer in western Germany” and published in the journal *Water Research* and the other one is titled “Atrazine soil core residue analysis from an agricultural field 21 years after its ban” and published in the *Journal of Environmental Quality*. The content structure of those articles was not adopted to this monograph, but implemented in a new uniform structure, what was possible due to their thematic reference. Formulations, Tables and Figures were adopted but partially modified. On the other hand additional information and important raw data were included in several places and in the appendix.

Table of Contents

Abbreviations and Symbols

ASE	accelerated solvent extraction
CEC_{eff}	cation exchange capacity (effective)
DAR	deethylatrazine to atrazine ratio
DEA	deethylatrazine
DIA	deisopropylatrazine
DOC	dissolved organic carbon
$t_{d,50}$	degradation time of 50%
EC	Specific electrical conductivity [$\mu S\ cm^{-1}$]
HPLC	high-performance liquid chromatography
K_d	sorption distribution coefficient [$L^3\ M^{-1}$]
K	hydraulic conductivity [$L\ T^{-1}$]
K_f	Freundlich sorption coefficient [$L^3\ M^{-1}$]
K_{oc}	organic carbon normalized distribution coefficient [$L^3\ M^{-1}$]
LC-MS/MS	liquid chromatography tandem mass spectrometry
LOQ	limits of quantification
OW	observation well
PC	principal component
PCA	principal component analysis
ROS	regression on order statistics
SPE	solid phase extraction
$T_{1/2}$	Half-life value [T]
WFD	water framework directive

List of Figures

List of Tables

1. Introduction

1.1 Atrazine in the environment

1.1.1 Background information

The s-triazine atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) was introduced in 1957 and is worldwide one of the most applied herbicides for weed control with 70,000 to 90,000 tons applied per year before its ban in the European Union in 2004 (Premazzi and Stecchi, 1990). Atrazine, a pre- and postemergent herbicide, inhibits the growth of target weeds by disturbing photosynthesis (Graymore et al., 2001). It is used mainly in maize monoculture, but also for sorghum, sugarcane, pineapple, other crops, conifer reforestation plantings, non-cropped industrial lands (e.g. railways), selected vegetable and cereal crops, vines, fruit orchards, citrus groves and grasslands (EXTOXNET, 1996, Graymore et al., 2001).

The persistence of a chemical in the environment is of highest importance, because with a longer residence time of a pollutant in nature, the exposure of susceptible non-target organisms or populations and accordingly the risk of harmful adverse effects increase. Although some persistent pesticides are not toxic in concentrations found in the environment, hazardous loads may be reached due to biomagnification in the food chain (Navarro et al., 2007). The potential of atrazine bioconcentration and biomagnification in the food chain is classified as “low” due to a low octanol-water partition coefficient (log K_{OW} = 2.7 at 25°C) and a rapid biological metabolism and elimination, resulting in bioconcentration factors generally less than 10 for the majority of tested species (Giddings et al., 2005). Accordingly, the importance of atrazine biomagnification in the food chain is negligible in contrast to its exposure through the water path, where atrazine is relatively persistent (Solomon et al., 2008). Accordingly, other studies pointed to the fact that atrazine holds endocrine disruptive effects on aquatic organisms, amphibians and reptiles and the risk of reproductive cancers for humans (Fan et al., 2007, Graymore et al., 2001),

Despite the fact that atrazine and its metabolites are highly recalcitrant in the environment and they are considered to be one of the main pollutants observed in groundwater bodies all over the world (Morvan et al., 2006, Tappe et al., 2002, Tesoriero et al., 2007), it is still allowed to be applied for weed control in many countries. In several of these countries - e.g. in South America - pesticide thresholds for ground- and drinking water and accordingly groundwater monitoring has not been introduced yet. Atrazine is also still frequently used in the USA where the threshold limit is 3.0 µg L^{-1} for ground and drinking water (USEPA, 2003), which is 30 times higher than the atrazine and single pesticide threshold limit for ground and drinking water in the European Union (EU, 1998). This big difference in threshold legislation between the countries of the European Union and the USA suggests rather an arbitrary decision making by the respective authorities than a uniform threshold determination with a common scientific basis including a precautionary principle. Consequently, monitoring of atrazine in the groundwater-soil environment is essential to limit its use and to take action in case of threshold-exceedances, accompanied by possible harmful effects on non-target individuals.

1.1.2 Atrazine in groundwaters

This intense use of atrazine frequently resulted in contaminations and exceedances of thresholds of ground and drinking waters, reported mainly in Europe (Gutierrez and Baran, 2009, Morvan et al., 2006, Tappe et al., 2002) and in North Armerica (Kolpin et al., 1998, Tesoriero et al., 2007, Thurman et al., 1998). In Europe pesticide concentrations in ground and drinking water must not exceed 0.1 µg L^{-1} for single compounds and 0.5 µg L^{-1} for the sum of all pesticides according to the European Council Directive 98/83/EC “The quality of water intended for human consumption” (1998). The European Water Framework Directive (WFD - 2000/60/EC, EU, 2000) established objectives to achieve a good quantitative and chemical status of groundwater bodies in 2015. Accordingly, analysis of contamination levels

and contaminant concentration trends are important to understand the fate of these compounds in the subsurface and to estimate whether contaminants fall below the European threshold. Monitoring of pollutants and quality parameters in groundwater is thus essential.

In Germany atrazine was banned in March 1991 due to findings of atrazine concentrations exceeding threshold values in ground and drinking water. Nevertheless, atrazine and the metabolite deethylatrazine were still detected in German aquifers more than 10 years after its prohibition, often without a considerable decreasing trend in groundwater concentrations (Tappe et al., 2002). These findings point at high persistence of atrazine in the soil-groundwater environment.

Atrazine was found to be more persistent in groundwater than in soils. This was assumed to be related to the i) lack of atrazine degrading microorganisms ii) a low organic carbon content which is a major factor determining the growth of the microorganism population that degrades atrazine co-metabolically (Barbash and Resek, 1996)) and iii) low oxygen contents in groundwaters (Schwab et al., 2006). However, Van der Pas et al. (1998) and Boesten and van der Pas (1993) observed that atrazine was degraded to some extend under saturated and sterile conditions with a low redox potential and reducing conditions respectively and referred this to reductive dechlorination. Accordingly, latter authors found much shorter half-life values for atrazine in saturated anaerobic sandy subsoil material collected below the groundwater table (0.2 to 0.3 years) than in the same but unsaturated and aerobic material (1 to > 5 years).

Metabolites

Several metabolites of atrazine were identified and three of them, deethylatrazine (DEA), deisopropylatrazine (DIA) and 2-hydroxyatrazine are considered to be key metabolites. Moreover DEA and DIA are categorized as `major´ and `relevant´ according to Directive 91/414/EEC (EU, 1991). This definition of a `relevant´ metabolite suggests i) properties similar in nature to those of the parent compound with respect to its biological target activity

or ii) severe toxicological properties or iii) a higher or comparable risk to non-target organisms than the parent compound. Accordingly, `major´ and `relevant´ metabolites should be taken into account for any risk assessment procedure. DEA and DIA are formed by dealkylation of the parent triazine. DEA emerges by deethylation from atrazine or propazine, whereas deisopropylation of atrazine, cyanazine or simazine produces DIA (Figure 1). These reaction pathways within soils have been described in earlier studies (Adams and Thurman, 1991, Mills and Thurman, 1994, Thurman et al., 1994, Thurman et al., 1998). In these studies DEA was reported to be the most common triazine metabolite in soils and groundwaters. The authors also stated that detection counts of DIA were generally much less than those of DEA. The reaction mechanism of deisopropylation was hypothesized to be 2-3 times slower compared to deethylation with regard to any parent triazine (Mills and Thurman, 1994). Additionally, further dealkylation of monodealkylated metabolites was observed in the subsoil, again with a preference for deethylation, hence leading generally to lower DIA concentrations in groundwater and soils (Mills and Thurman, 1994).

The physico-chemical properties of metabolites can clearly differ from those of their parent compounds. Correspondingly, K_{OC}-values for atrazine (K_{OC} = 160) are much higher than for DEA (K_{OC} = 16) and for DIA (K_{OC} = 5) (Thurman et al., 1998). Accordingly, atrazine was reported to adsorb to the soil matrix more strongly than deethylatrazine and found with average soil concentration being four times higher than the average concentration of DEA (Adams and Thurman, 1991). Hence DEA is transported through the vadose zone faster than atrazine. To characterize atrazine transport in soils, the deethylatrazine to atrazine ratio (DAR) was introduced (Adams and Thurman, 1991). During transport through the unsaturated zone, atrazine is gradually deethylated, with slower infiltration increasing the time for metabolic dealkylation of atrazine. As degradation of atrazine to DEA is primarily the result of metabolic activity of soil bacteria and fungi, atrazine could be (co-)metabolized in significant amounts by soil microorganisms when dispersed in the environment equably on the field-scale. This would increase the DAR. In contrast, in case of a point-source contamination, where atrazine could enter an aquifer more directly via natural or artificial

conduits (DeMartinis and Royce, 1990), the contact time between atrazine and the soil microorganisms is very short. Hence the DAR should be significantly less than unity. For example, Thurman et al. (1998) linked findings of DAR values of smaller than 0.3 with point-source contaminations. Accordingly the DAR is a helpful tool to distinguish between atrazine point- and nonpoint-source contaminations. The approach to evaluate point-source versus nonpoint-source pollution using the DAR is based on the premise that atrazine degradation is negligible in aquifers, because of aforementioned low organic C concentrations, small microbial populations and low oxygen contents.

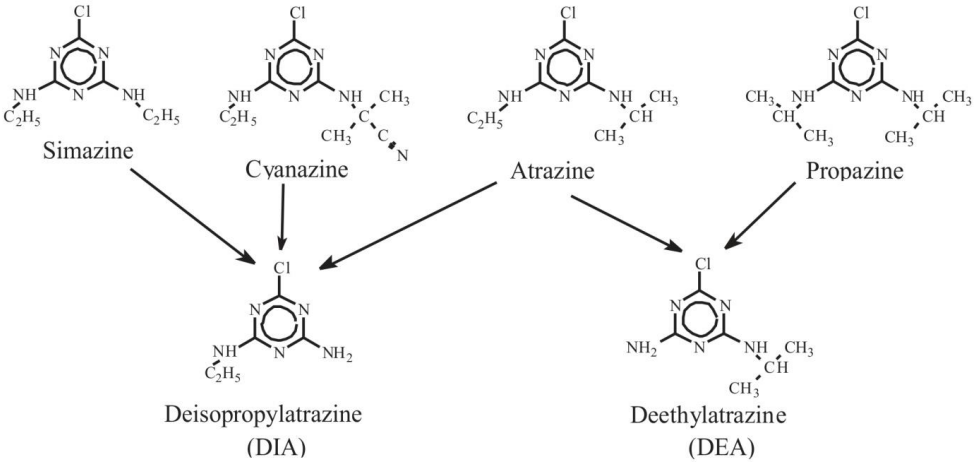


Figure 1: Degradation pathways for the triazines atrazine, simazine, propazine, and simazine to deethylatrazine and/or deisopropylatrazine, according to Thurman et al. (1994).

1.1.3 Atrazine and its metabolites in soils

Atrazine findings in groundwater a long time after its ban with partly increasing concentration trends, as reviewed above, suggest that atrazine adsorbed or bound to soil particles might be mobilized on the long term and lead to a loading of groundwater. Supporting this assumption, a long-term field lysimeter study showed that 22 years after the last atrazine application, extracted atrazine corresponded with soil adsorbed concentrations

of 1 µg kg^{-1} in the top layer, indicating a potential risk of successive groundwater contamination by remobilization and leaching on the long term (Jablonowski et al., 2009).

The distribution of atrazine between solid particles and pore water is a key parameter that determines its mobility and decay in porous media. In soils the major adsorbing surfaces for atrazine are located on soil organic matter (Lima et al., 2010), which is most important for atrazine sorption in topsoils and on clay minerals (Herwig et al., 2001), which are more important in subsurface soil layers (Vryzas et al., 2007). In contrast, atrazine sorption on to Fe-oxides was reported to be negligible (Clausen and Fabricius, 2001). The soil organic matter content is considered to be the most important factor governing atrazine bound or non-extractable residue formation, which primarily occurs in the soil particle size fraction <20 µm (Loiseau and Barriuso, 2002).

Basic concepts of atrazine sorption to organic matter suggest nonspecific hydrophobic interactions with aliphatic and aromatic compounds; specific interactions namely H-bonding to carboxylic and phenolic groups, and ligand exchange (Chefetz et al., 2004, Spark and Swift, 2002). For bound- or non-extractable residues covalent bonds between the pollutant and organic matter and entrapment or sequestration of the compound in voids of the soil organic matter and clays were identified to be the main mechanisms (Dec and Bollag, 1997, Gevao et al., 2001, Loiseau and Barriuso, 2002). Since the aged pesticide residues are more resistant to biodegradation and extraction (Hatzinger and Alexander, 1995, Pignatello and Xing, 1996, Scribner et al., 1992), a repeated application of pesticides may lead to the buildup of residues and the “bound residues” fraction. Despite of not being extractable, a release of bound residues might be possible on the long term, facilitated by the activity of microorganisms, a change in agricultural practice and the introduction of other chemicals that may change the biochemistry of soils (Gevao et al., 2000). Extractable residues, which were analyzed in this study, might be released even more easily compared to bound residues due to weaker sorption states. Accordingly, both atrazine bound and extractable residues may have relevant environmental consequences, of which one is a continuous and prolonged leaching to groundwater.

Clay minerals are the inorganic soil constituents with the highest sorption capacity for positively charged compounds due to net negative surface charges and a high surface area. Herbicides like s-triazines are known to adsorb to clays as protonated or neutral species according to pH-controlled compound speciation (Weber, 1970). When the pH of the solution approximates or is below the pK_a of the compound, it gets protonated and adsorbs to clay minerals. Atrazine is a weak base with a pk_a of 1.7 and therefore protonation at pH ≥ 4 is negligible. Hence sorption of the protonated atrazine species in agricultural soils seems to be of minor importance. However, it was reported that on the surface of clay minerals the pH value is 0.5 to 4 units below the pH value of the bulk solution (Bailey et al., 1968, Herwig et al., 2001, Weber, 1970), what significantly increases the sorption potential on to clay minerals, in particular that of 2-hydroxyatrazine (pK_a: 4.6), because a significant fraction of atrazine and 2-hydroxyatrazine would be protonated in agricultural soils. Accordingly, Vryzas et al., (2007) reported that atrazine and 2-hydroxyatrazine Freundlich sorption coefficients, K_f, increased for atrazine and 2-hydroxyatrazine with decreasing pH (from 8 to 6) for subsurface soils, where the adsorption potential is mainly affected by clay content.

In numerous studies the degradation behavior of atrazine in soil environments has been investigated. Atrazine $t_{d,50}$ values of field studies range from a few days to 108 days and for lab studies up to 150 days (PPDB, 2013). Other laboratory experiments presented a wider range of atrazine half-life values in topsoils from 5 (Vryzas et al., 2012a) to 433 days (Charnay et al., 2005) and for subsurface soils from 43 (Vryzas et al., 2012a), 231 to 407 days (Accinelli et al., 2001) to over 900 days (Blume et al., 2004), generally showing higher half-life values with increasing depth (Accinelli et al., 2001, Blume et al., 2004, Kruger et al., 1993). These highly differing half-life and $t_{d,50}$ values are due to individual biological and chemico-physical properties of various soils and to different methodical approaches. The study of Jablonowski et al. (2009) showed that an atrazine half-life value of one year highly underestimates residual soil atrazine aged for 22 years under outdoor conditions. Estimations of long-term herbicide accumulation, persistence and release may be inaccurate when using first-order degradation kinetics with $t_{d,50}$ values that were derived from short-term

experiments. Confirming this, Vryzas et al., (2012b) stated a high initial dissipation of atrazine after application (5 < $t_{d,50}$ < 18 days) followed by an increase in persistence after four months. Generally, pesticide half-life values for subsurface soil samples are higher than those of surface soil samples which was correlated to a decrease in soil biomass with increasing soil depth and an accordingly slow biological degradation (Accinelli et al., 2001, Vryzas et al., 2012a). Additionally, atrazine degradation and bioaccumulation in the rhizosphere was also found to be associated with ryegrass cultivation, which activated atrazine degrading enzymes (Sui and Yang, 2013). This indicates that pesticide residues in the lower parts of soil profiles might be more persistent. However, Kruger et al. (1997) found that atrazine degradation increased in subsurface soil samples when being saturated ($t_{d,50}$ = 53 days) in contrast to unsaturated soil samples ($t_{d,50}$ = 204 days). This was related to a larger fraction of atrazine in wetter than in drier soils that is dissolved in the soil solution and bioavailable. However, the change from aerobic to anaerobic conditions accompanied by a change of redox potential to reducing conditions when soils are saturated reduces the degradation rate of atrazine due to a decreased microbial activity (Blume et al., 2004, Schwab et al., 2006). Atrazine degradation in groundwater affected subsoils was found to increase from unsaturated aerobic to unsaturated reducing conditions, what was attributed to reductive dechlorination (Boesten et al., 1993, van der Pas et al., 1998). Hence, atrazine might be degraded by reductive dechlorination in the part of the subsoil that is influenced by groundwater table fluctuations. On the other hand, when herbicides are not or slowly degraded in the groundwater, herbicides may be laterally transported by the groundwater flow. This lateral transport may generate higher herbicide concentrations in the groundwater affected subsoil than in the overlaying soil layers.

1.2 Study objectives

The overall objective of this study is to investigate the occurrence and concentration trends of atrazine and its main metabolites in the groundwater-soil environment after the

prohibition of its use. Data of two decades of monitoring of the Zwischenscholle aquifer and soil residue analysis 21 years after its ban were analyzed.

The main goals of the atrazine groundwater monitoring study, accounting for the demands of the Water Framework Directive, were to i) characterize the temporal and spatial variability of atrazine concentrations in a shallow phreatic aquifer body, ii) analyze atrazine concentration trends, iii) identify relationships between monitored groundwater quality parameters, iv) characterize atrazine and metabolite transport and v) finally assessing the long term persistence of atrazine and its metabolites in the groundwater based on unique long-term monitoring data collected for 20 years after atrazine was banned in 1991.

The objective of atrazine soil core residue analysis was to check, if significant amounts of atrazine residues are still present in the unsaturated zone 21 years after its ban and how these residues are distributed in the soil profile down to the groundwater table. Based on the atrazine residue profiles in the unsaturated zone, it was aimed at evaluating to which extent persistent concentration of high levels of atrazine that were monitored in the underlying aquifer could be due to subsequent supply of atrazine from the unsaturated zone and potentially might contribute to sustain atrazine concentrations in this aquifer. Therefore soil core samples from an agricultural field in the Zwischenscholle study area, which was part of the PEGASE project (Pesticides in European Groundwaters: detailed study of representative Aquifers and Simulation of possible Evolution scenarios; EU contract number EVK1-CT1999-00028) (Mouvet et al., 2004) and in which atrazine groundwater concentrations were monitored (Vonberg et al., 2014), were investigated in this study.

2. Study area

2.1 Regional and geologic setting

The study area (Figure 2, Figure 3) is located near Jülich in the Lower Rhine Embayment, which reaches from the Variscian Folded Mountains in the south to its tectonic lengthening of the Dutch Rift Valley in the north. In the west it borders to the “westlichen Randstaffeln” and part of the Northern Eifel and in the east to the “Bergisches Land” and the upper cretaceous basin of the Münsterland (Münsterländische Oberkreidemulde). Since Tertiarian times, it is an area of ongoing subsidence accompanied by several northwest-southeast striking faults separating miscellaneous geologic horsts, rifts or half-graben (Walter, 1995). Accordingly the Zwischenscholle represents one of the various geologic half-graben structures, which are separated by several northwest-southeast striking faults and thus is surrounded by the Rurscholle separated by the Rursprung fault in the southwest and by the Erftscholle separated by the Rurrand fault in the northeast (Figure 2 and Figure 3). The Zwischenscholle is lowered with respect to the Erftscholle and lifted with respect to the Rurscholle. Sediments of approximately 1200 m and up to 100 m thickness for Tertiary and Quaternary times respectively have been deposited since the beginning of subsidence on top of the base of Variscian folded sediments of the Devonian and Carboniferous times (Walter, 1995). The quaternary sediments in the southern part of the Lower Rhine Embayment, where the Zwischenscholle study area is located, are mainly glacio-fluvial or fluvial deposits of the Meuse and Rhine river systems (Klostermann, 1992).

2.2 Hydrogeology

The upper Zwischenscholle aquifer, corresponding to layers 16/14 of the lithostratigraphic unit catalogue of Schneider and Thiele (1965), which is the study object of this project, is a mixture of unconfined and semiconfined quaternary Rhine and Meuse

sediments, characterized mainly as sandy and gravelly (Klostermann, 1992). It is bounded in the northeast by the Rurrand fault which acts as a natural no flux boundary. In the southern part, the aquifer is hydraulically connected through the Rursprung fault zone to the aquifer of the Rurscholle. The aquifer base is the water impermeable Reuver clay, layer 11 (Schneider and Thiele, 1965). Figure 2 shows groundwater isohypses and drying areas, which represent sections of the aquifer 16/14 either influenced by dewatering for open pit mining or natural marginal groundwater thickness. Accordingly, the aquifer thickness varies between 1 m in the northwest of the Forschungszentrum Jülich area, 15 m in the southwest and more than 30 m in the northeast close to the Rurrand fault zone, with an average of 10.9 m (Jahn, 2002). Shallow depths to the groundwater table (0.9 m to 8 m; except for 30 m close to the Rurrand fault zone) are reported. The groundwater flow direction is approximately from southeast to northwest with a mean hydraulic gradient between 0.1 % and 0.2 % and a porosity ranging from 20 % to 30 % (Lahmeyer International, 1984).

In the study of Jahn (2002) hydraulic conductivity (K-) values were calculated using geologic layer information provided by the company RWE Rheinbraun. For this purpose, an analysis of descriptive statistics of K values of single subdivisions of the upper Zwischenscholle aquifer 16/14 were conducted by averaging their K values and weighting them according to layer thickness. Statistical analysis reveals an arithmetic mean of $2.11 \cdot 10^{-3}$ m s^{-1}. The distribution of calculated K-values is bimodal and made up by two lognormal distributions (data not shown). The first peak of the distribution corresponds with a K of $1.23 \cdot 10^{-4}$m s^{-1} (upper range: $3.35 \cdot 10^{-4}$; lower range: $4.54 \cdot 10^{-5}$) and the second with a K of $1.11 \cdot 10^{-2}$ m s^{-1} (upper range: $5.0 \cdot 10^{-2}$; lower range: $2.48 \cdot 10^{-3}$). The bimodal distribution of K-values is caused by the presence of sand and silt lenses within mainly gravel media. These data point at an important heterogeneity of the aquifer.

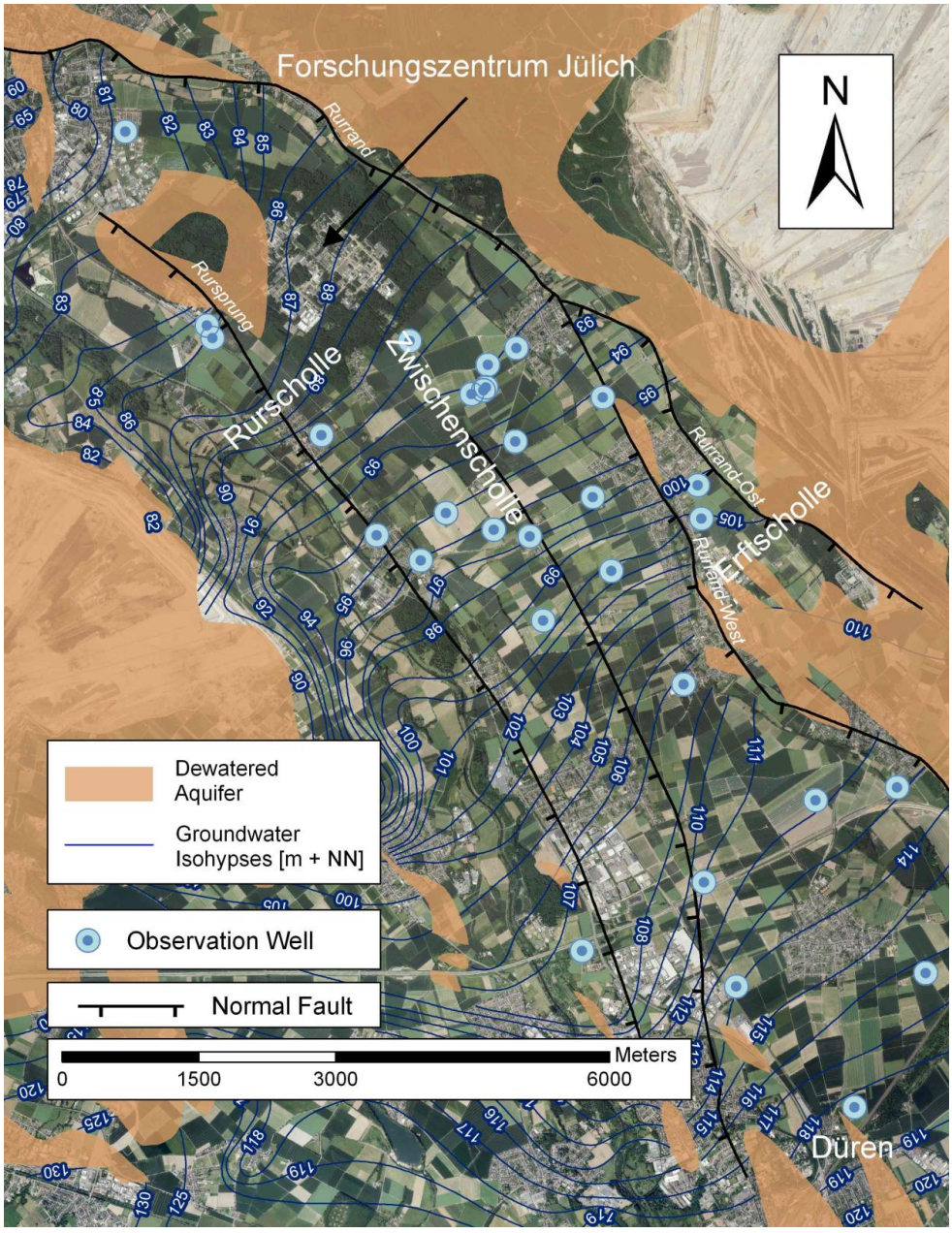


Figure 2: Digital orthographic pictures of the Zwischenscholle study area (Geobasis NRW, 2014) showing basically agricultural land use, normal faults of the Lower Rhine Embayment, positions of groundwater observation wells, and groundwater isohypses.

2.3 Soils and land use

The study area is part of the Jülicher Börde, characterized by loess sediments. Most abundant soil types are Cambisol, Luvisols, stagnic Luvisols, Gleysols and Fluvisols (as defined by the World reference base for soil resources (FAO, 2006). The land use is mainly agriculture, whereas the area framing the Forschungszentrum Jülich is forested. Minor areas are urban sealed surfaces. In times prior to the ban of atrazine, typical crop rotation was sugar beet and winter wheat. Potatoes, oat and maize were marginally cultivated. Between 1983 and 1993 the fractions of the total agricultural land taken by the different crops were on average: 50% winter wheat; 35 % sugar beet, 8 % pasture; 4 % maize and 3 % potato cultivation. Atrazine was potentially applied in maize fields until it was banned in 1991.

Due to short transport distances in the vadose zone down to the groundwater and intensive agricultural land use, the vulnerability of the Zwischenscholle aquifer to pesticide contamination is considered high (Herbst et al., 2005). It should however be noted that the area, which was cultivated with maize and where atrazine was applied was small.

3. Material & Methods

3.1 Groundwater monitoring

3.1.1 Monitoring principles

In total 60 observation wells (OWs), tapping the first shallow aquifer (layers 16/14 (Schneider and Thiele, 1965)) of the Zwischenscholle, were included in groundwater quality monitoring since 1991. Over a period of two decades, the selection of sampled OWs changed. In case of negligible pesticide findings at specific OWs, the groundwater sampling frequency was reduced in some cases or sampling was stopped. However, some OWs with constant low atrazine concentrations (20219, 20220, 20251, 20266 and 20267) are still frequently sampled. In OWs with high contamination levels, sampling was kept constant. Distinctive changes of selected OWs are indicated by vertical dashed lines in Figure 5 (chapter 4.1.3, page 54). Sampling frequencies were generally low in the time between 1991 and 2003 and limited to a few sampling campaigns (1991/1992, 2000/2001, 2002/2003). In 2005 monthly sampling of 19 OWs was introduced, recently reduced to 11 OWs. The filter depth with reference to groundwater surface is highly variable and ranges from 0 m to 14.2 m (mean: 4.7 m). The filter screen lengths vary between 1 m and 10 m (mean: 3.1 m). Groundwater sampling was done by the Agrosphere Institute (IBG-3) and the local water management service company ”Erftverband” according to guidelines of the Deutsche Vereinigung für Wasserwirtschaft Abwasser und Abfall (DWA, 2011). Groundwater sample analyses were done by the Erftverband. In total 36 pesticides and 6 physico-chemical parameters were routinely analyzed. The temperature, specific electrical conductivity, pH, and redox potential were measured in situ during groundwater sampling, nitrate contents were determined by the Erftverband and DOC analysis was done by the Agrosphere Institute.

3.1.2 Pesticide Analytics - Sample treatment and analysis

Since 2000, groundwater samples were analyzed according to the DIN EN ISO 11369 (1997a) work instruction by the Erftverband. A high-performance liquid chromatograph (HPLC) (Shimadzu LC-10AD vp) equipped with a UV-detector (Photo diode array detector, Shimadzu SPD-M10A$_{VP}$) was used. Prior to quantification of substance concentrations via gradient-elution, groundwater samples were concentrated via solid phase extraction (SPE). OASIS HLB (30 µm, 3cc, 60 mg) cartridges were used for SPE procedures. Sample treatment and analysis are explained in the following:

A) *Conditioning and analyte enrichment*: i) three times washing of SPE cartridges with acetone, ii) three times washing with double distilled water, keeping the water in the cartridge after the third time and iii) letting one liter of groundwater sample flow through the cartridge with a rate of 1 L h^{-1}. *B) Washing:* three times washing with double distilled water and subsequently drying of the adsorbent with a nitrogen flow for 30 minutes. *C) Elution:* Analytes were eluted two times with 2 mL and one time with 1 mL of Acetone with residence times of 15 minutes, respectively. Eluates were concentrated with nitrogen flow until dryness. *D) Sample analysis preparation:* dried eluates were solved in 0.5 mL of water (A) and acetonitrile (B) (80/20, v/v), according to initial conditions of the HPLC gradient program.

For chromatography an ODS-Hypersil column, 125 x 2.1 mm and 3 µm particle size was used. The program of gradient elution was: 0 min—80% A and 20 % B; 16 min—70% A and 30% B; 34 min—50% A and 50% B; 39 min—100% B; 50 min—100% B; 54 min—80% A and 20% B; 75 min— 80% A and 20 % B, the flow rate was 0.19 mL min^{-1}. Retention times of analyzed compounds were: atrazine: 18.31 min; deethylatrazine: 5.52 min; deisopropylatrazine: 3.23 min; simazine: 12.02 min; diurone: 20.25 min; propazine: 25.30 min and terbuthlyazine: 27.53 min. The analytical wavelength used for quantification of analytes was 220 nm for atrazine, terbuthlyazine, simazine and propazine; 214 nm for DEA and DIA; and 245 nm for diuron. A compound was considered as detected when the retention time of the compound was in accordance with the retention time of the respective

standard compound and when their UV-spectra were in agreement by > 95%. The limits of quantification (LOQ) for the respective analytes were: *atrazine*: 0.011 µg L^{-1}; *deethylatrazine*: 0.038 µg L^{-1}; *deisopropylatrazine*: 0.04 µg L^{-1}; *diuron*: 0.05 µg L^{-1}; *propazine*: 0.046 µg L^{-1}; *simazine*: 0.027 µg L^{-1}; *terbuthylazine*: 0.031 µg L^{-1} and. It was not documented in the database if monitored chemicals were detectable or only < LOQ. Hence non-quantifiable analyte concentrations were treated as < LOQ.

The analysis of groundwater samples in 1991/1992 was done externally and detailed information about used equipment is not available. Therefore these data are only shown as additional information to the time series of groundwater concentrations that were obtained later. These data were however not used in other analyses like the principal component analyses.

3.1.3 Laboratory reporting limits & Data Censoring

Quantification of contaminants in groundwater is limited due to analytical methods. In the low concentration range, contaminants cannot be quantified below the limit of quantification (LOQ). The Erftverband set the official LOQ of pesticide analytics to 0.05 µg L^{-1} (half of the threshold of 0.1 µg L^{-1}). Due to the accuracy of the equipment, a LOQ <0.05 µg L^{-1} was reached. Dependent on the agent dealing with analytical data, pesticide concentration data were either reported using the official LOQ of 0.05 µg L^{-1} or using the actual, equipment dependent LOQ. The fraction of measurements below the laboratory reporting limit or LOQ is called “nondetects”, or “censored data” (Helsel, 2012) because the only information about these values is that they are somewhere between zero and the LOQ. However, in this study the term “nonquantifiable values” is used to avoid a confusion of the analytical thresholds “limit of detection” and “limit of quantification”, because in this study “nonquantifiable values” refer to the data fraction of groundwater sample analysis below the limit of quantification, without distinguishing values smaller than the LOQ from measurements without any detectable analyte concentrations (< limit of detection, LOD). In this study, the fraction of

nonquantifiable values of all atrazine measurements from 1991 to 2012 accounted for 41.6%. When computing descriptive statistics, the fraction of nonquantifiable values complicates this procedure and an approach need to be found how to deal with them. A fatal approach is just to ignore nonquantifiable values and only considering quantified values for statistical analysis. This creates a strong upward bias for statistical parameters like the mean and the median. Other – more common – practices are substituting nonquantifiable values by either half of the quantification limit, and less frequently the LOQ itself or also by zero (Helsel, 2010, 2012). However, this kind of data treatment was reported to produce less reliable estimates of descriptive statistics, especially when substituting nonquantifiable values by zero or by the LOQ, causing stronger artificial biases on descriptive statistics than nonquantifiable values substitutions by half of the LOQ. To reduce the bias on e.g. the calculated mean from a data set in which nonquantifiable values are substituted by a fixed value, e.g. Helsel (2010, 2012) discussed several alternative methods that estimate the concentration distribution for the nonquantifiable values fraction, e.g. the maximum likelihood estimations (MLE) and the "regression on order statistics" (ROS). The robust form of ROS was used in this study because it avoids transformation bias for log-transformed data.

The (ROS) method is based on least squares regression on a normal probability plot. The "robust" implementation of ROS uses the uncensored (detects) fraction of the data that are transformed to a normal distribution based on an assumption about their distribution. The censored values are predicted by the respective regression model. The resulting dataset combining uncensored observations and imputed estimates for censored values is used for computing summary statistics. This method is especially efficient for datasets exhibiting a lognormal distribution and which are transformed accordingly prior to performing the ROS fit.

All data censoring procedures were carried out using R and the NADA library (Helsel, 2010).

In this study, all datasets were checked for their distribution and in most cases log-transformation was applied to obtain a shape closer to normal distribution. Atrazine concentration data was not censored using ROS for small datasets ($n < 10$), where substitution of nonquantifiable values was recommended by (Farnham et al., 2002).

3.1.4 Atrazine concentration trend analysis

A simple classification of atrazine concentration trends as “increasing” or “decreasing” and in case of insufficient significance as “no trend” was aspired for each observation well for time series data since 2000. For this purpose, atrazine concentration data since 2000 was analyzed by least squares linear regression fits and its slope was used for classifying the atrazine concentration trend.

The coefficient of determination (r^2) expresses the goodness of the linear regression fit by expressing the fraction of variability of a dependent variable (here atrazine concentration) explained by the linear model. In general, the closer the value of r^2 is to one, the better the linear regression fit. In cases of small r^2 values the validity of the linear fit and hence the validity of the respective atrazine concentration trend can be tested by the F-Test. For this purpose it is tested, if the value of the coefficient of determination is by chance or not. The null hypothesis, which says that the coefficient of determination of the least squares regression fit is zero (H_0: $R^2 = 0$) or that there is no linear relationship, is tested. The p-value (probability value) indicates the probability to obtain a given random sample in case of a valid null hypothesis. P-values range between zero and one, for zero indicating a negligible exceedances probability under a valid null hypothesis. The null hypothesis can be rejected if the p-value is smaller than the significance level α ($p \leq \alpha$; here: $\alpha = 0.05$). If the null hypothesis is rejected, it can be stated that the regression model is significant and the slope of the fitted linear regression reflects the direction of the atrazine concentration trend for a significance level $\alpha = 0.05$.

F-test calculations were conducted using OriginPro 8G software.

3.1.5 Principal Component Analysis

Complex datasets comprised of pollutants like pesticides and a large number of physico-chemical parameters, are often difficult to analyze and interpret. The multivariate statistical

technique PCA can be a helpful tool to find relationships between monitored parameters and hence to improve understanding of environmental quality. The Principal Component Analysis (PCA) was already applied with respect to groundwater pollution by agricultural activity by e.g. Melo et al. (2012) and Ielpo et al. (2012) and reviewed by Olsen et al. (2012).

The PCA method basically reduces a dataset of *n* variables, i.e. analytical parameters to a new dataset with *m* orthogonal (uncorrelated) variables which are the principle components (PCs). These PCs are ordered from PC1 to PC*m* with decreasing explained variance of the original dataset. The approach establishes a covariance matrix, its eigenvalues and eigenvectors. The eigenvalues are equal to the explained variance and the eigenvectors consist of the PC coefficients or weights, extracted from the covariance matrix. The intention is to explain most of the dataset variance with the smallest possible number of first PCs. This is the case when high correlations between variables are present.

Multiplying the PC coefficients by the square root of the eigenvalues results in a *n* x *m* matrix of the so called loadings, which reflect the contribution of an original variable to the respective PC. Furthermore, multiplying the loadings matrix with the original data record vectors results in new data record values, called scores, which represent the coordinates of this record in the PC coordinate system.

The groundwater monitoring data was implemented in an ACCESS database and individual compositions of variables for different PCA runs were extracted by EXCEL.

3.1.5.1 Data treatment

Prior to performing PCA-runs, the data was treated according to standard procedures reviewed in Olsen et al. (2012), which are explained in the following. Since a PCA requires a complete data record, some variables from the dataset were excluded to retain a sufficiently large number of data records. Although DIA and simazine were not detected in a large number of samples (83% and 73%, Table 1) these variables were retained in the dataset because of their importance for the subject of variable correlations. The variables filter depth and/or groundwater table depth were first included in PCA runs but did not show any

correlation to atrazine concentrations or DAR values and reduced the quality of PCA results significantly (data not shown). Therefore, these variables were excluded from the PCA analysis.

A number of 450 data records of originally 1208 (Table 1) were complete and included in the PCA. For the PCA nonquantifiable values were substituted by half the quantification limit, a common data treatment procedure of nonquantifiable values for PCA (Olsen et al., 2012). Data was checked for skewness and log-transformation was applied in many cases to obtain an unskewed distribution as recommended by Legendre and Legendre (2006). An outlier check was not considered. All variables were normalized, i.e. generating a zero mean and a standard deviation of one to eliminate the influence of absolute values of the various variables. All PCA runs were conducted using MATLAB.

Table 1: Data summary for principle component analysis (PCA).

	Atrazine	DEA	DIA	Simazine	Diuron	Propazine	Nitrate	EC	DOC
Number of Samples	1208	1180	1173	1189	1170	1079	991	911	699
Nondetects [%]	42.3	42.1	83.3	73.1	86.1	70.9	4.8	-	2.86
Missing data [%]	4.5	6.7	7.3	6.01	7.5	14.7	21.7	28.0	44.7

3.2 Atrazine residue analysis of soil core samples

3.2.1 Soil samples and application history

For analysis of atrazine residues, soil samples were taken from an agricultural field site, where atrazine was applied before the ban in 1991 (Krauthausen soil A, KS-A-1-3, Figure 3). The soils of the sampling sites can be classified as Ultisols and gleyed Inceptisols using USDA Soil Taxonomy (USDA, 1999) or as Gleysols and gleyic Cambisols according to the World Reference Base for Soil Resources (FAO, 2006). Krauthausen A was the only field

with an atrazine application history that could be identified, because before its ban in 1991 documentation of applied pesticides was not mandatory so that for information about application doses one is completely dependent on the cooperation, memory and availability of farmers who were active before 1991. The frequency of atrazine application was not documented and is therefore not accurately known. According to the farmer who cultivated the field, atrazine was applied in total 2 to 3 times, when corn was planted. The recommended atrazine application dose of 0.96 to 1 kg ha^{-1} was applied. However, partially doses up to 3 kg ha^{-1} were allowed. The KS-A samples were taken by drilling to a depth of 3 m using a probe head diameter of 85 mm. The groundwater table was located at 231 cm (KS-A-1), 280 cm (KS-A-2) and > 300 cm, (KS-A-3) below surface. The soil cores were divided into 8 sections (0-10 cm, 10-30 cm, 30-60 cm, 60-100 cm, 100-150 cm, 150-200 cm, 200-250 cm and >250 cm) for atrazine residue analysis.

Soil samples from another field site at Krauthausen (Krauthausen soil B, KS-B) with unknown atrazine application history were used for testing the method performance of accelerated solvent extractions and subsequent LC-MS/MS analysis in the low atrazine concentration range ≤ 0.1 μg kg^{-1}. The KS-B soil was collected with a Humax manual drill-probe (Martin Burch AG) to 30 cm depth. Eight Samples were randomly taken and combined afterwards.

At a third field close to Selhausen without atrazine application history, soil samples were taken from the top layer (0-10 cm) (Selhausen soil, SeS) for determining the extraction recovery using a spike-experiment. SeS soil samples were taken from the top layer (0-10 cm).

All soil samples were dried at 40°C, sieved < 2 mm and further homogenized for 20 minutes at 200 rpm using a planetary ball mill (PM 400, Retsch) prior to accelerated solvent extraction. A soil bulk density of 1.5 g cm^{-3} was assumed for atrazine residue calculations.

3.2.2 Soil characteristics

For soil characterization, pH value, effective cation exchange capacity (CEC), grain size distribution and organic carbon content (C_{org}) were determined for one soil core representative (KS-A-3) for the respective agricultural field. The pH-values were measured, mixing 10 g of soil with 25 mL of a 0.01 M $CaCl_2$ solution. The effective CEC was determined in accordance to Mehlich (1945) and DIN ISO 13536:1997-04 (1997b). Dried and pre-sieved (< 2 mm) soil samples were analyzed for grain size distribution of sand (2000-63 μm), silt (63-2 μm), and clay (<2 μm) by Agfa-Labs (Coulter LS13320 – Tornado with a Dry Powder Module). C_{org} was measured with a Multiphase Carbon and Hydrogen / Moisture Analyzer (RC 612, Leco).

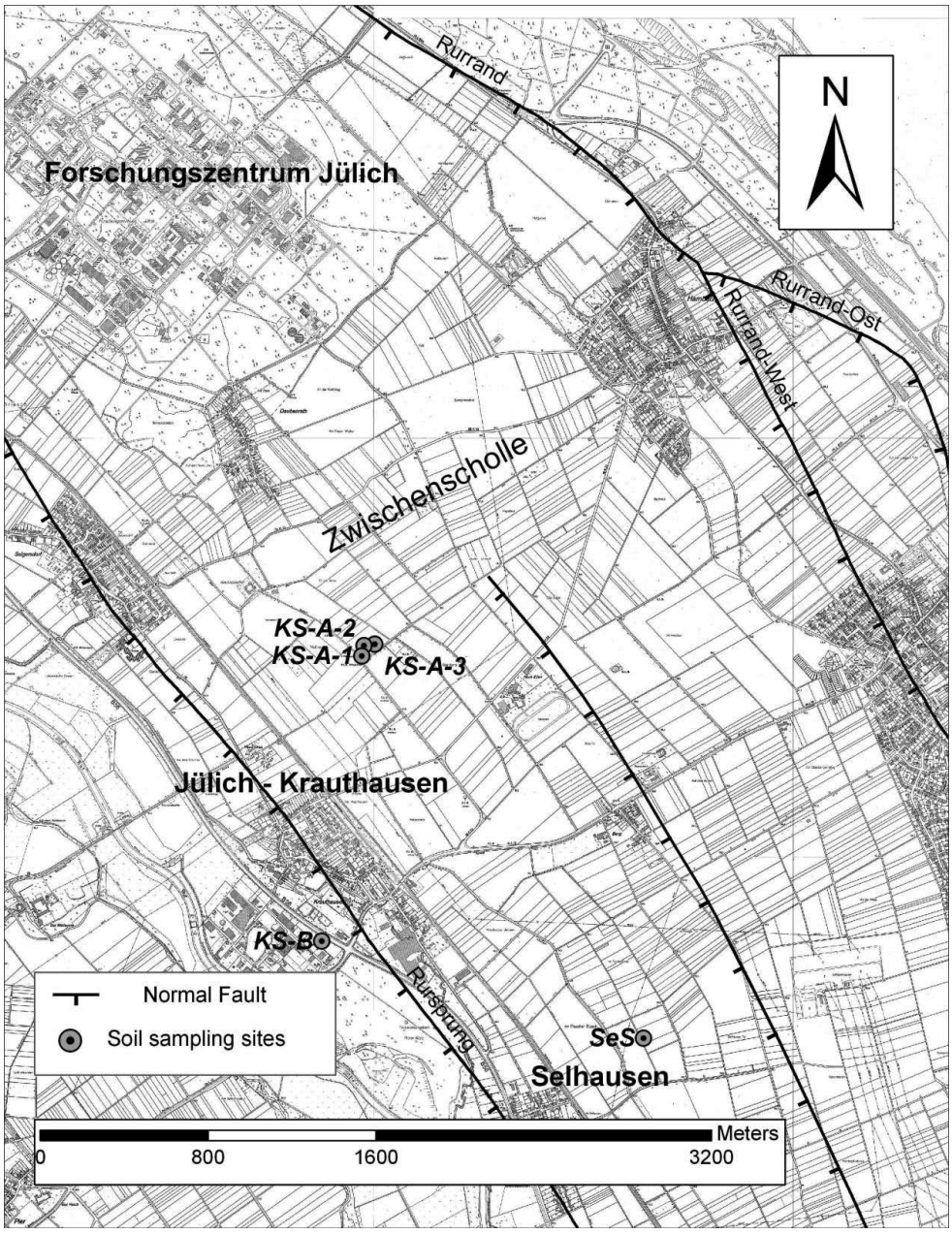


Figure 3: Topographic map of the Zwischenscholle study area with soil sampling sites and normal faults.

3.2.3 Chemicals

Atrazine (99%) (Riedel-de Haën, Seelze, Germany), and 2-hydroxyatrazine (Dr. Ehrenstorfer GmbH, Germany) were used for spiking and extraction recovery experiments, deuterated (D_5)-atrazine (99%) and (D_5)-2-hydroxyatrazine (97%) (Dr. Ehrenstorfer GmbH, Germany) as internal standards for LC-MS/MS measurements, diatomaceous earth for ASE extractions of soils (Thermo Scientific), water (MilliQ plus 185, Millipore, Molsheim, France) acidified with formic acid (Merck, suprapur) and methanol (Biosolve, ULC/MS quality) as eluents for LC-MS/MS analysis and methanol (BDH Prolabo, 99.8%) for ASE.

3.2.4 Accelerated solvent extraction

A Dionex ASE 200 device was used for accelerated solvent extractions (ASE). ASE methods for atrazine extractions were described earlier by Gan et al. (1999) and Jablonowski et al. (2009). According to Jablonowski et al. (2009) we used a methanol/water solution (4:1, v:v) as extraction solvent.

For extractions, triplicates of 10 g of homogenized soil were weighed in 11 mL stainless steel ASE cells. For better extraction efficiency and to avoid clogging of ASE steel filter lids, the ASE cells were additionally filled with diatomaceous earth (Dionex). The extraction pressure and temperature were first optimized for extracting the Krauthausen soil (KS-A) using extraction pressure and temperature combinations of 100, 150 and 206.8 bar with each 100°C and 135°C. Further extraction parameters: a flush volume of 60% of ASE cell volume (6.6 mL), a heat-up time of 5 min, static time of 15 min and cell purging of 100 s using nitrogen gas were adjusted according to Jablonowski et al. (2009).

3.2.5 Triazine extraction recovery

For the determination of the extraction efficiency, spiking experiments with SeS soil were conducted. Systematic matrix effects of different soil matrices within a soil profile on atrazine recovery could not be observed in an earlier study (Dagnac et al., 2005). Thus we only used topsoil with the highest C_{org} content to optimize the overall extraction efficiency. SeS samples

were spiked at two concentration levels of 1.0 µg kg^{-1} and 0.1 µg kg^{-1} with atrazine and 2-hydroxyatrazine. For spiking, two separate solutions (0.01 µg mL^{-1} and 0.001 µg mL^{-1}) were prepared out of stock solutions with each 10 µg mL^{-1} for atrazine and 2-hydroxyatrazine, respectively. 100 g of dried soil was spiked with 10 mL spiking-solution. After one hour, soil samples were homogenized and subsequently extracted in triplicates using the ASE and analyzed by LC-MS/MS. To account for background contamination, additional blanks of SeS samples were extracted.

This extraction recovery test yield cannot be compared with the extraction yield of aged triazine soil residues, where a certain fraction of the adsorbed chemical is either in a stronger sorption state like covalent bonding or fixated in inaccessible parts of the soil matrix, resulting in a lower remobilization potential, as already discussed in chapter 1.1.3.

3.2.6 LC-MS/MS analysis

Liquid extracts were analyzed for atrazine and 2-hydroxyatrazine using a Thermo Electron Model TSQ-Quantum equipped with CTC-HTC-PAL sampler, coupled with a HPLC with binary pump and column oven (25°C, Agilent Serie 1100). Deuterated (D_5)-atrazine and (D_5)-2-hydroxyatrazine were used as internal standards for quantification, with a concentration of 0.01 µg mL^{-1} each: prior to LC-MS/MS measurement, each 10 µl of the D_5 standard solution were added to 100 µL of the ASE extract. A MZ PerfectSil Target ODS-3 (125 mm x 2.1 mm x 3 µm) column was used with a flow rate of 0.15 mL min^{-1} and 25°C column temperature. For LC gradient elution a mixture of a 0.1% aqueous formic acid solution (A) and methanol (B) was used. The program of gradient elution was: 0 min – 95% A, 15 min – 95% A, 20 min – 80% A, 25 min – 60% A, 30 min – 10% A, 33 min – 0% A, 43 min – 0% A, 45 min – 95% A, 50 min – 95% A. This long elution time of was used here to avoid quenching of the atrazine peak by co-extracted matrix compounds and thus allow quantification of lowest atrazine concentrations (for details see Appendix B: Accelerated Solvent Extraction (ASE) and LC-MS/MS method validation). The retention times of atrazine and 2-hydroxyatrazine were 32.14 min and 30.65 min, respectively. The separated

compounds were ionized in positive electrospray (ESI+) mode and transitions to 3 product ions each were measured: for atrazine (m/z of 216 Da) the product ions exhibited a m/z ratio of i) 174.2 Da, ii) 103.9 Da and iii) 131.9 Da; for 2-hydroxyatrazine (m/z of 198 Da) product ions exhibited a m/z ratio of i) 156 Da, ii) 114 Da and iii) 86 Da. The analysis of two additional product ions served as qualifiers for compound identification. The characteristic ratios of product ion peak areas for atrazine, 2-hydroxyatrazine, deuterated D_5-atrazine and D_5-2-hydroxyatrazine were previously determined by directly injecting a solution with a concentration of 0.1 µg mL^{-1} with a flow rate of 25 µl min^{-1} in the MS/MS instrument, respectively. LC-MS/MS analyses were generally performed in duplicate and total injection volume for each sample was 10 µl.

The limit of quantification (LOQ) for LC-MS/MS analysis was 0.01 ng mL^{-1} for both analytes, corresponding to 0.015 ± 0.002 µg kg^{-1} soil adsorbed atrazine and 2-hydroxyatrazine (based on a mean extract volume of 15.2 mL with a standard deviation of 1.63 mL for 54 measurements) per 10 g of extracted dry soil). Further concentration of extracts could even improve the quantification limit of corresponding soil adsorbed atrazine concentration, if needed.

4. Results & Discussion

4.1 Groundwater monitoring

4.1.1 Groundwater chemistry

Measurements of selected physico-chemical parameters were summarized in Table 2. High mean values for the specific electrical conductivity and nitrate, even exceeding the threshold for nitrate in ground- and drinking waters (50 mg/L), indicate a distinct impact of agriculture. The electrical conductivity measured in observation wells at agricultural field sites of the Zwischenscholle increased about 47 % from 1975 to 1992, which was explained by intensified agriculture (Lingelbach, 1996), Unpublished results). The range of Redox-Potential values indicates that conditions vary between slightly reducing and slightly aerobic.

Table 2: Means and ranges for parameters of groundwater chemistry of the Zwischenscholle aquifer, analyzed for monthly taken groundwater samples of observation wells shown in Figure 4 since 2005.

Parameter	Range	Arithmetic mean	Number of samples
Specific electrical conductivity [µS/cm]	282 – 921	735	817
pH	5.41 – 8.1	6.7	324[a]
Redox-Potential [mV]	-70 – 319	184	694[a]
Nitrate [mg/l]	<LOQ[b]. – 153	53	895
Dissolved Organic Carbon (DOC) [mg/l]	<LOQ[b]. – 77	4.61	895

[a] Measurements of pH and Redox-Potential were irregularly and completely stopped in 1/2008.
[b] Limit of quantification (LOQ) for nitrate and DOC are 0.1 mg mL^{-1} and 0.5 mg L^{-1}, respectively.

4.1.2 Data Censoring using "regression on order statistics" (ROS)

In order to test the ROS method estimating means of censored data, the entire dataset of atrazine and deethylatrazine, respectively, was considered and censored using artificial LOQs (0.05 µg L^{-1} and 0.1 µg L^{-1}) that were higher than the true LOQs (Table 3). The means

estimated from the artificially censored data using ROS were compared with the means calculated from the true dataset to evaluate the effect of censoring and applying the ROS for estimating means. Additionally, to demonstrate the effect of substitution, nonquantifiable values were substituted by i) zero and ii) the LOQ. The respective atrazine means of i) 0.072 µg L^{-1} and ii) 0.078 µg L^{-1} (Table 3) indicate that in this case atrazine means are overestimated for higher censoring limits and thus for datasets with higher fractions of nonquantifiable values (58 % and 75 %, respectively) compared to the mean of 0.064 µg L^{-1} using real LOQs (43 % nonquantifiable values). The difference between the normal distribution and the distribution of log transformed atrazine concentrations of the artificially censored datasets with higher fractions of nonquantifiable values (Table 3) apparently led to an overestimation of the true mean by the ROS estimated mean. The goodness-of-fit measures (R^2) which even increase for artificial censored datasets with higher LOQ concentrations (Table 4, page 64) do not reflect here the accuracy of estimated values for nonquantifiable values. Therefore, the mean atrazine concentrations obtained with the ROS method may be considered to be a conservative estimate of the true mean atrazine concentration. For deethylatrazine all ROS based means for different LOQs are almost equal, even for the artificially censored dataset using an LOQ of 0.1 µg L^{-1} what points at a good approximation of the distribution of log-transformed concentration by a normal distribution. In this case, even the artificially increased high fraction of nonquantifiable values (83 %) does not significantly decrease the accuracy of the estimated mean atrazine concentration values compared to real LOQ and 0.05 µg L^{-1} LOQ censored datasets. A small portion of the data is therefore enough to reflect the distributional shape. Both examples show that the validity of ROS based models predicting nonquantifiable analyte concentrations depend primarily on the distributional shape of transformed or non-transformed concentrations and its similarity to the normal distribution, which is used by the model to predict nonquantifiable values. The relevance of the fraction of nonquantifiable values as indicator for the validity of estimated values is thus dependent of the distributional shape of concentration values.

To show the differences between distributions of ROS censored data and of datasets in which nonquantifiable values were substituted by the half of the limit of quantification, distributions obtained by both approaches were presented in Figure 6. For datasets with more than 50 % of nonquantifiable values, the median, 25th percentile, and lower range of the substituted dataset are equal to LOQ/2 (Figure 6b) whereas for the ROS censored datasets these values are derived from the distribution of estimated concentrations (Figure 6a).

Table 3: Application of ROS – data censoring technique for all measurements from 1991 to 2011 of atrazine and deethylatrazine, respectively, are presented. Different letters indicate significant differences of atrazine concentration means for a significance level of 0.05, using Tukey test.

Data Treatment	**Atrazine mean [µg L^{-1}]**	**95 % Confidence Interval**	**Fraction of Nonquantifiable Values**
Substitution : 0	0.059 a	0.054 – 0.063	43 %
Substitution: LOQ	0.067 b	0.063 – 0.072	43 %
ROS (real LOQ, range: 0.01 – 0.05 µg L^{-1})	0.064 b	0.060 – 0.068	43 %
ROS (LOQ = 0.05 µg L^{-1})	0.072 bc	0.068 – 0.076	58 %
ROS (LOQ = 0.10 µg L^{-1})	0.078 c	0.074 – 0.082	75 %
	DEA mean [µg L^{-1}]		
Substitution : 0	0.048 a	0.043 – 0.052	42 %
Substitution: LOQ	0.064 b	0.060 – 0.067	42 %
ROS (real LOQ, 0.038 – 0.05 µg L^{-1})	0.057 b	0.053 – 0.061	42 %
ROS (LOQ = 0.05 µg L^{-1})	0.058 b	0.054 – 0.062	59 %
ROS (LOQ = 0.10 µg L^{-1})	0.057 b	0.053 – 0.061	83 %

4.1.3 Summary statistics of monitoring data

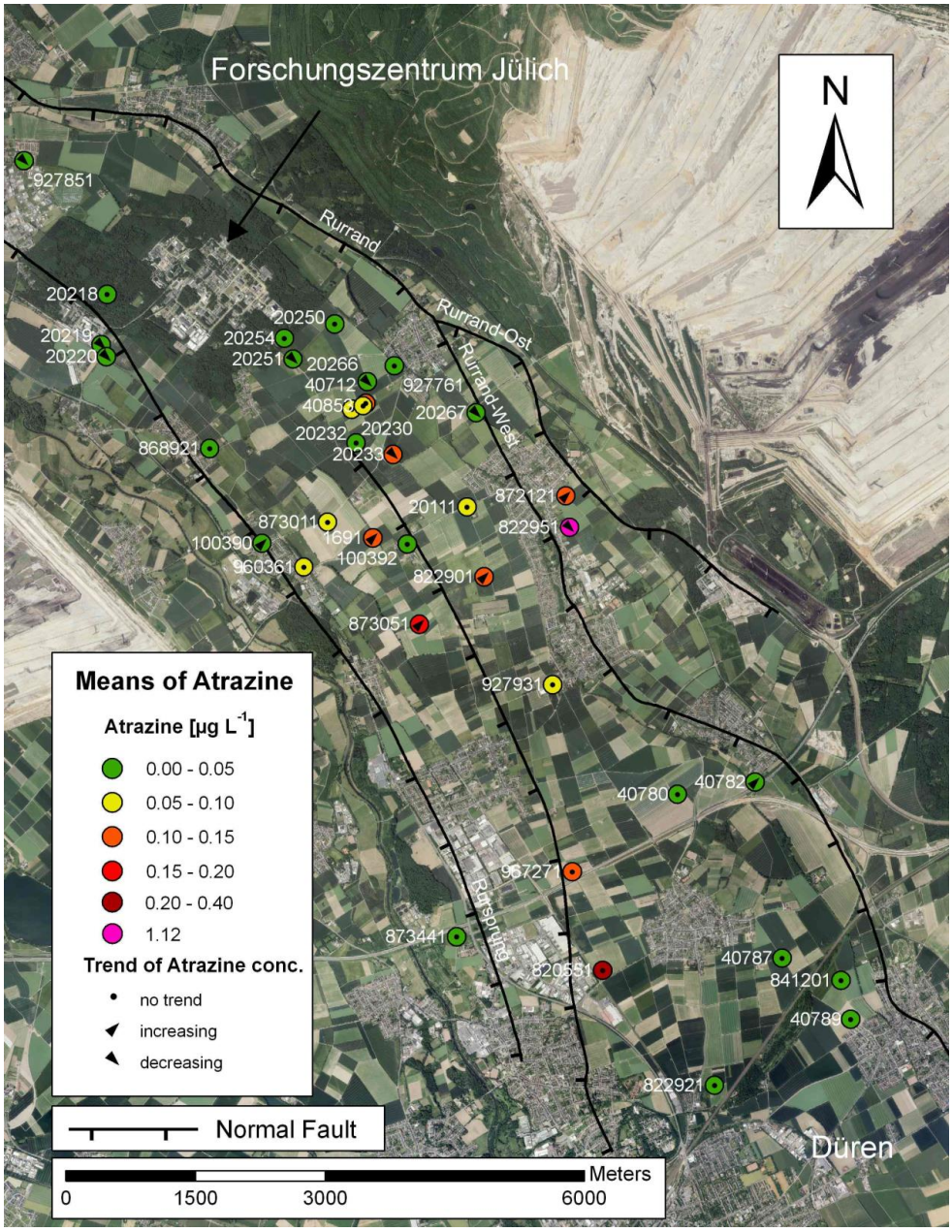


Figure 4: Study area (Geobasis NRW, 2014) and observation wells with their mean atrazine concentration during the sampling period and the concentration trend since 2000 (significance level of F-test to linear regressions, $p < 0.05$, for details see Table 14).

An overview of mean atrazine concentrations of combined observed and modeled (estimates of nonquantifiable) values in the monitored wells are shown in Figure 4. For the different years, distributions of atrazine concentration data (observed and modeled) are shown in Figure 5 (page 54) and Figure 6 (logarithmic concentration plot, page 55). Model output data of linear regressions of uncensored observations used for the estimation of concentration values for nonquantifiable values are shown in Table 4 (page 65), Table 5 (structure of atrazine concentration datasets, page 66) and in Figure 9 (Kernel density distribution functions and probability/normal quantile plots of linear regressions, page 60-64). Generally, the goodness-of-fit-measures or R^2 values of the linear models are high, frequently with values higher than 0.9 or in few cases, higher than 0.7. The estimated model coefficients with relative low standard errors were highly significant mainly on a level $\alpha = 0.000$, using t-tests. The goodness of these model parameters is a prerequisite of the model estimating nonquantifiable values adequately.

However, in two cases, models cannot be classified as valid, due to nonsignificant parameters (1991/1992) and due to a fraction of nonquantifiable values of 85% (OW 20266). In these cases, estimates for nonquantifiable values cannot be considered reliable just like the resulting summary statistics. Computing summary statistics using substitutes for nonquantifiable values also leads to non-reliable results in this case due to high fractions of nonquantifiable values.

Since 2000, the concentration distributions do not show a consistent change over time. It must however be noted that the wells that were monitored changed over time (indicated by vertical dashed lines in Figure 5 and Figure 6) and that wells in which no pesticides were detected were either sampled less regularly or excluded from and that some additional wells were included in the monitoring program over time. Therefore, it is not possible to make conclusive statements about the change of atrazine concentrations in the aquifer. This becomes particularly obvious considering the change in sampled observation wells from the campaign of 1991/1992 to 2000 (Figure 5 and Figure 6). Here for example, 10 OWs with

mostly negligible atrazine concentrations were excluded and 13 new OWs, in which higher atrazine concentrations were detected (e.g. 1691, 20111, 40853), were included in 2000. Accordingly a strong increase in mean atrazine concentrations from 0.02 µg L^{-1} (1991/1992, non-reliable) to 0.07 µg L^{-1} (2000) can be assumed and is mainly due to the change in the selection of observation wells. However, it must be mentioned that a direct comparison of the results of 1991/1992 and the following campaigns should also be avoided due to the unknown analytical equipment used in the period of 1991/1992 besides of non-reliable estimates for nonquantifiable values.

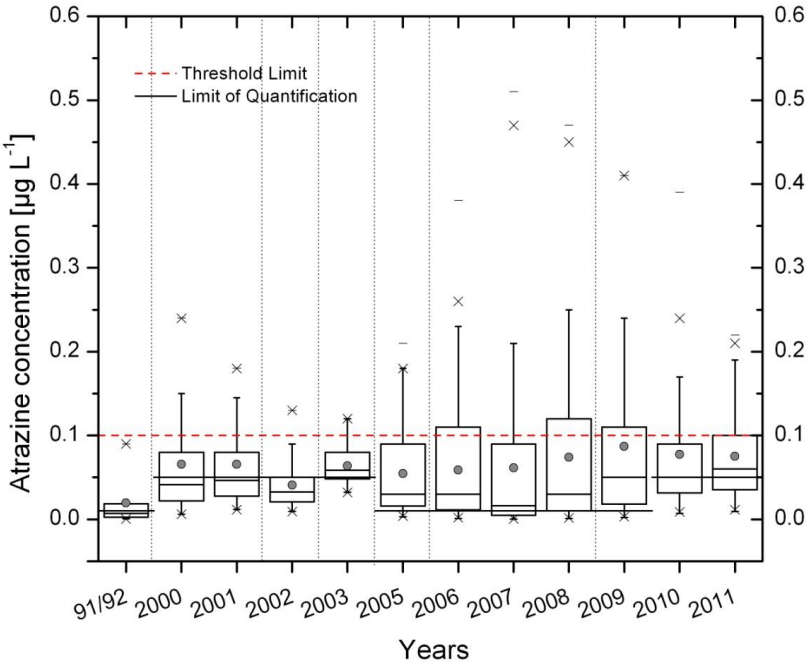


Figure 5: Annual descriptive statistics of atrazine including all measurements of all observation wells for the respective year using regression on order statistics (ROS). Boxplots show: range (-), 99th and 1st percentile (x), Whisker (1.5 x interquartile range), Box (interquartile range), median (solid horizontal line) and mean (dot). The horizontal solid lines represent the time dependent limit of quantification (LOQ). In 2010 the equipment dependent LOQ of 0.01 µg L^{-1} was changed to 0.05 µg L^{-1} due to the reasons given in chapter 3.3. The dashed vertical lines indicate a distinctive change in the selection of sampled OWs.

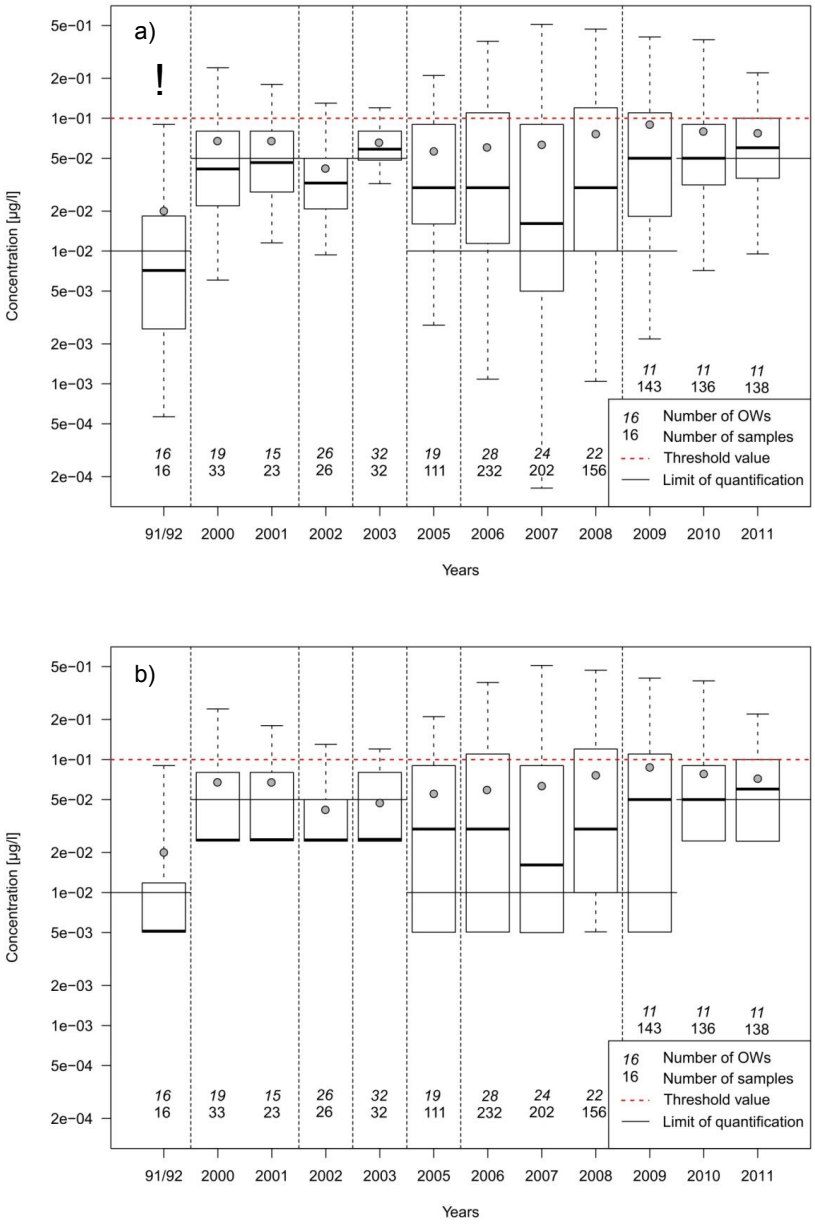


Figure 6: Annual descriptive statistics of atrazine including all measurements of all observation wells for the respective year using regression of order statistics (ROS) (a) or replacing the non-detects by LOQ/2 (b). Boxplots represent range, interquartile range, median (solid horizontal line) and mean (dot). The horizontal solid lines represent the time dependent limit of quantification (LOQ). In 2010 the equipment dependent LOQ of 0.01 µg L^{-1} was changed to 0.05 µg L^{-1} due to the reasons given in chapter 3.3. The dashed vertical lines indicate a distinctive change in the selection of sampled OWs.
! indicates non-reliable summary statistics due to nonsignificant model parameters used for estimating nonquantifiable values.

Over the last 10 years, the mean of atrazine concentrations in the groundwater samples did not change considerably and did not exceed the threshold value (e.g. Figure 5). However, when looking at atrazine concentrations in individual wells (Figure 4 and Figure 7), there is quite some variability between the different wells. In some wells the long term mean is above the threshold value whereas in other wells, pesticide concentrations are almost negligible (Figure 7). Accordingly, a considerable spatial variability in atrazine concentration distribution with a wide range of mean concentrations from n.d. or < LOQ to 1.12 µg L^{-1} is apparent.

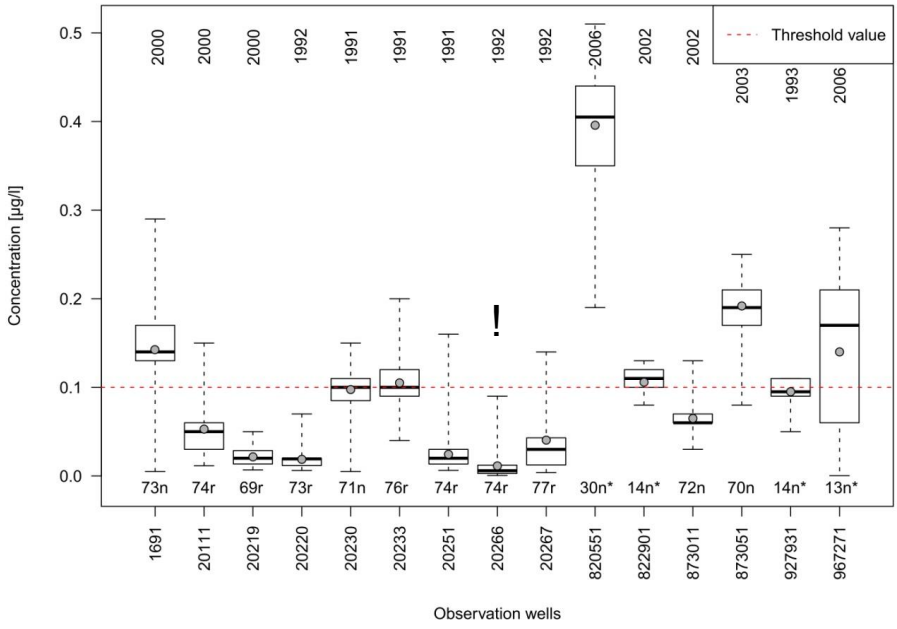


Figure 7: Boxplots of atrazine concentrations in observation wells which are sampled until today, or in which sampling restarted in 10/2012, indicated by "". The numbers in the base line indicate the respective total amount of samples for each OW, "r" means ROS censored data, "n" means non-censored data because of less than 4 nonquantifiable values which were simply substituted by half of the LOQ. In the top line, the year of first sampling for each OW is given.
! indicates non-reliable summary statistics due to a fraction of nonquantifiable values > 80 %, what is assessed as tenuous for the estimation of nonquantifiable values (Helsel, 2012).

The temporal evolution of atrazine and its metabolites also differs between the OWs. For the last years, atrazine concentrations show either a constant, an upward or a downward trend in different wells (Figure 10: 20230, 873051, 20233, page 69-71), also indicated by arrows (Figure 4), which reflect positive or negative slopes confirmed by F-Tests.

The calculated catchment zone of an observation well in the Zwischenscholle aquifer based on the approach expressed in Equation 1 reaches between 3800 m and 6080 m upstream (Figure 8), assuming homogeneously distributed mean aquifer properties (K = 2.11E-03 m s^{-1}, gradient: 0.2 %) a mean distance between the groundwater level and the upper and lower part of the filter of, respectively, 5 m and 8 m, and a mean groundwater recharge of 0.175 m a^{-1} (Bogena et al., 2005).

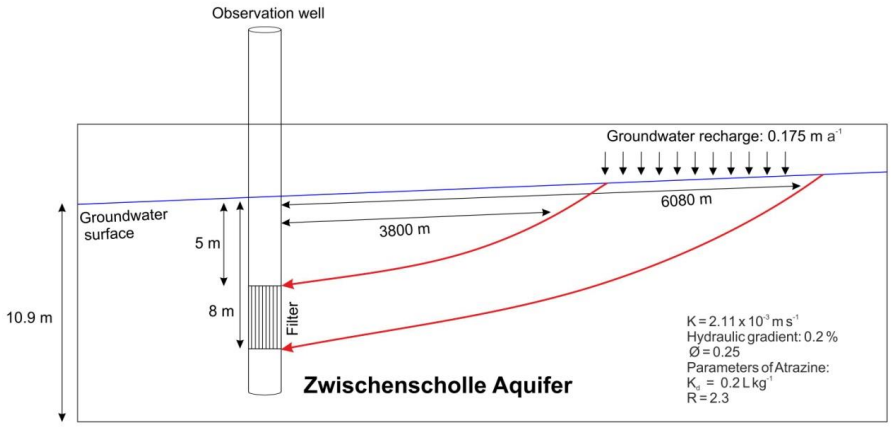


Figure 8: Catchment zone of an observation well for mean aquifer and observation well properties of the Zwischenscholle study area.

$$\boldsymbol{K} \times \boldsymbol{L_F} \times \boldsymbol{i} = \boldsymbol{GWR} \times \boldsymbol{L} \qquad \textbf{Equation 1}$$

L_F = Flow length between groundwater surface and depth of lower filter, i = gradient, GWR = groundwater recharge, L = Length of catchment zone

Accordingly, the calculation for the idealized catchment zone was conducted as follows: i) the lower and upper limit of the catchment zone expressed as distance [m] from the observation well correspond to

$$L = \frac{66541 \text{ m a}^{-1} \times 5\ m \times 0.002}{0.175\ m\ a^{-1}} \approx 3800\ m, \text{ and } L = \frac{66541 \text{ m a}^{-1} \times 8\ m \times 0.002}{0.175\ m\ a^{-1}} \approx 6080\ m,$$

respectively. This is an indication for the location of possible atrazine source zones and their contribution to atrazine detections at respective observation wells. Accordingly, there are

OWs, where atrazine findings might be associated with the same source zone (e.g. 820551 and 967271 or 873051 and 1691, 873011), considering a groundwater flow direction from southeast to northwest. In contrast the more local, high heterogeneous concentration distribution in OWs 20230, 20232, 20233, 20266, 40712 and 40853 (Figure 4) shows that different catchment zones are present.

A simple sample calculation shows that the groundwater of the Zwischenscholle aquifer – assuming mean aquifer properties (thickness: 10.9 m, porosity: 0.25) and a groundwater recharge like given above is completely exchanged after 15.5 years. For the Krauthausen study site which is part of the Zwischenscholle aquifer, atrazine K_d-values of 0.17 and 0.22 L kg^{-1} were determined (Mouvet et al., 2004). Assuming a K_d-value of 0.2 L kg^{-1} and thus a retardation factor of 2.3, an atrazine residence time of 35.3 years is calculated. Continuing high atrazine concentrations and locally upward concentration trends even 20 years after the ban of atrazine suggest long-term leaching from the vadose zone, sorption of atrazine to aquifer sediment and/or ongoing illegal inputs.

Previously, atrazine degradation was detected neither in sandy aerobic (Klint et al., 1993) nor in anaerobic aquifers (Arildskov et al., 2001, Rugge et al., 1999) which is in line with our findings of slowly decreasing, long term stable, or even increasing atrazine concentrations in groundwater samples. However, in anaerobic aquifers atrazine degradation might be significantly higher than in aerobic aquifers (Boesten et al., 1993, van der Pas et al., 1998). Latter authors found much shorter half-life values for atrazine (0.2 to 0.3 years) in saturated anaerobic sandy aquifer sediments than in aerobic ones (1 to > 5 years) and related this to either a comparatively high organic matter content or reductive dechlorination, for redox values around 70 to 110 mV. This reductive dechlorination is reported not to occur at redox potential values of 210 mV or higher (van der Pas et al., 1998), indicating medium aerobic conditions. In our study the mean value for the redox potential is 183 mV (-70 to 319 mV). Accordingly reductive dechlorination might be of minor or local importance in the mainly aerobic Zwischenscholle aquifer, corresponding to the high persistence of atrazine as mentioned above. However, in OWs 868921 and 927851, the only OWs with negative redox

potential values between -30 and -70 mV, atrazine is not detected. Either atrazine was degraded due to reductive dechlorination or it was never present due to the heterogeneous concentration distribution. Conversely, OW 927931 with a mean redox value of 74 mV has a comparatively high mean concentration of 0.095 µg L^{-1}. Obviously atrazine degradation due to reductive dechlorination is here of minor relevance.

Aerobic biotic transformation in aquifers might be strongly limited due to small microbial densities that correspond with a lack of available carbon or low DOC concentrations, which are required for the co-metabolic degradation of atrazine (Barbash and Resek, 1996). According to this, Perry (1990) calculated a half-life value for atrazine in a Kansas aquifer of 1000 days.

Detects of DIA and simazine were always observed simultaneous (Figure 10). Besides atrazine also cyanazine, propazine, and simazine can degrade in soil to both to DIA and DEA (Thurman et al., 1998). Thus, DIA concentrations may also be related to high simazine concentrations. Conversely, OWs without DIA findings neither showed any detection of simazine. OW 820551 (Figure 10), on the one hand exhibits high atrazine concentrations accompanied by DEA whereas on the other hand simazine and DIA concentrations at a lower level close to the threshold value were found. This again points to relations between simazine and DIA on the one hand and atrazine and DEA on the other hand. The correlation between simazine and DIA becomes also clear in the principle component analysis (chapter 4.1.6, page 75), whereas Pearson correlation coefficients between concentrations of atrazine and DIA (r = 0.43) and simazine and DIA (0.63) of the complete database do not clearly point out this correlation.

Fig. 9a

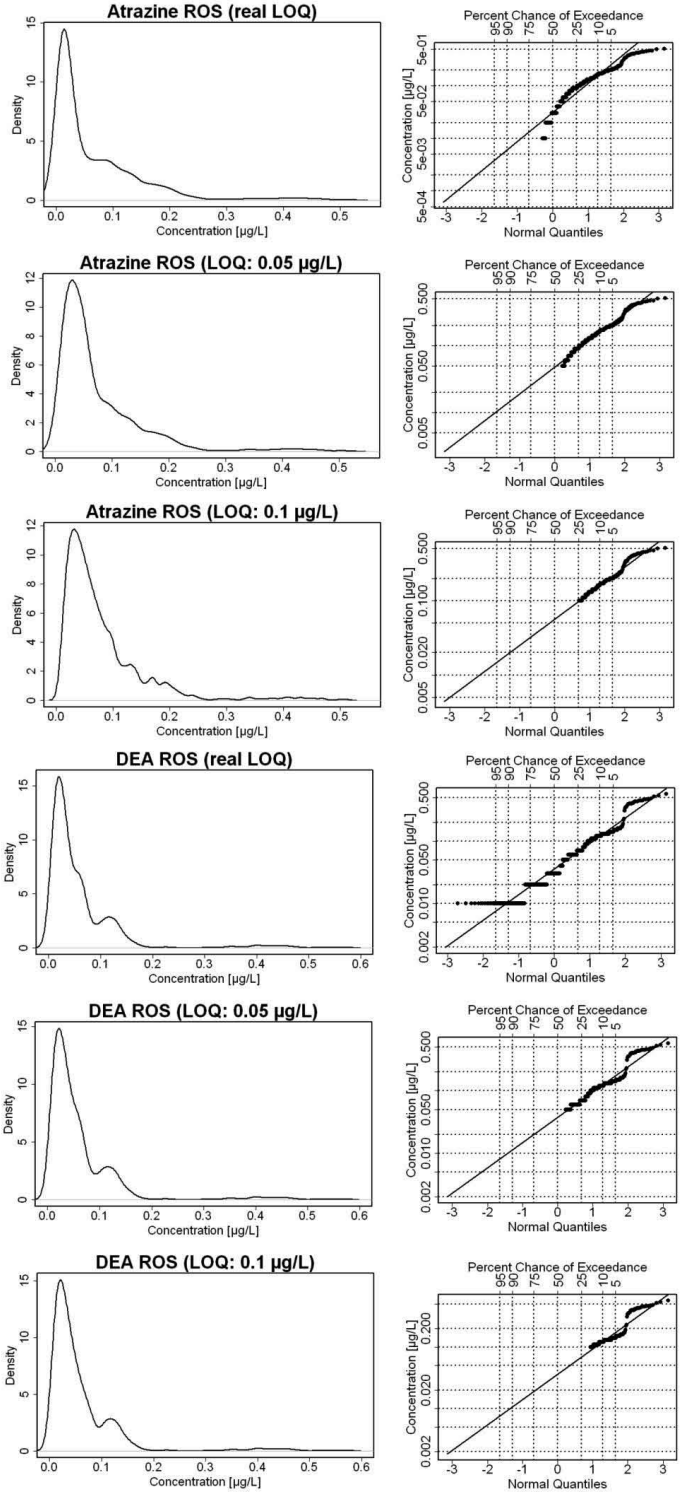

Atrazine ROS (real LOQ)
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
Atrazine ROS (LOQ: 0.05 µg/L)
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
Atrazine ROS (LOQ: 0.1 µg/L)
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
DEA ROS (real LOQ)
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
DEA ROS (LOQ: 0.05 µg/L)
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
DEA ROS (LOQ: 0.1 µg/L)
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles

Fig. 9b

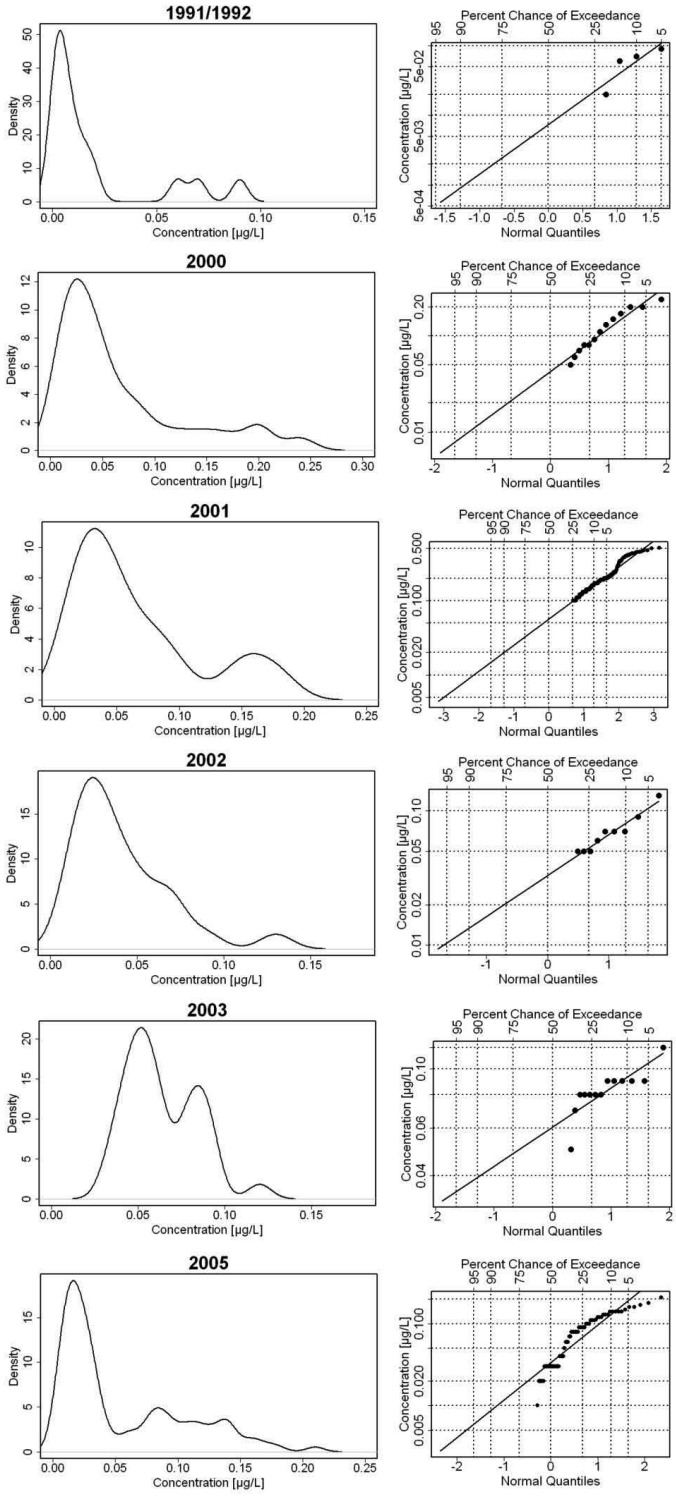

1991/1992
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
2000
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
2001
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
2002
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
2003
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
2005
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles

Fig. 9c

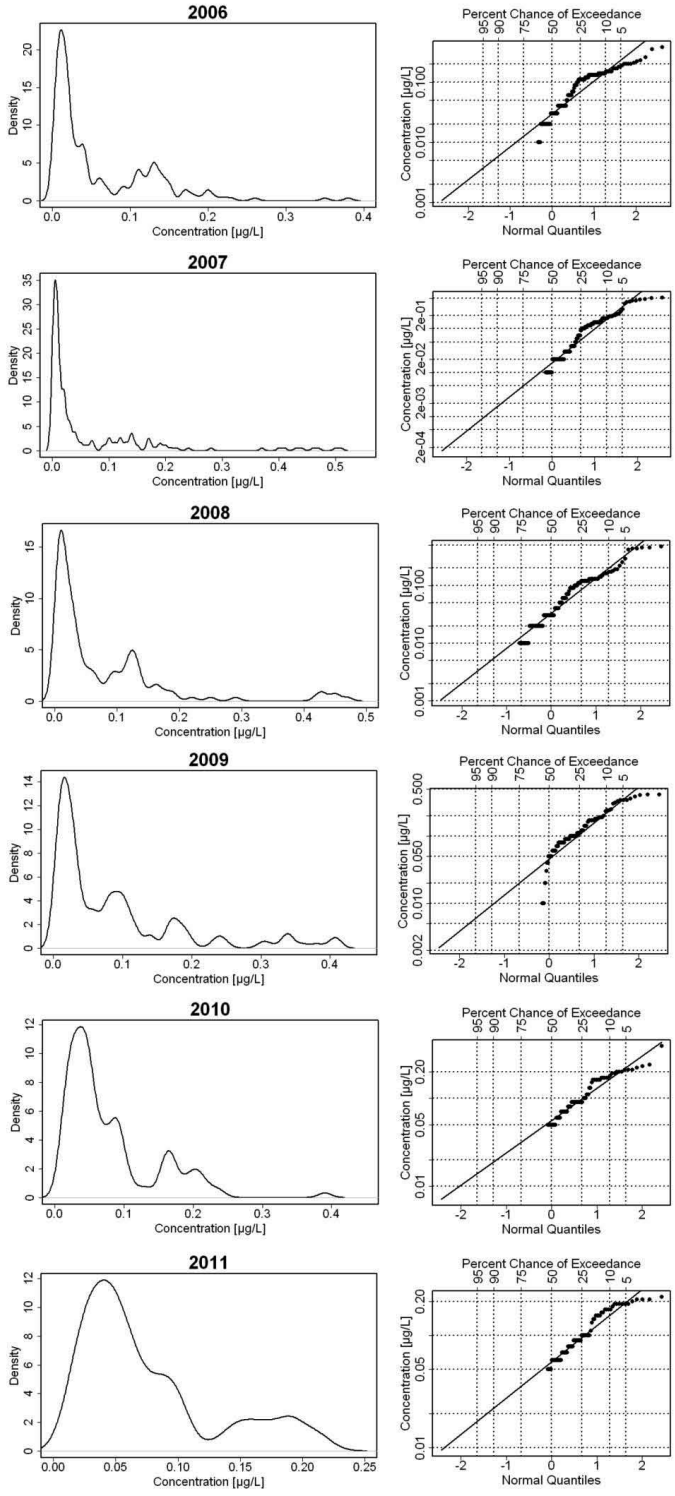
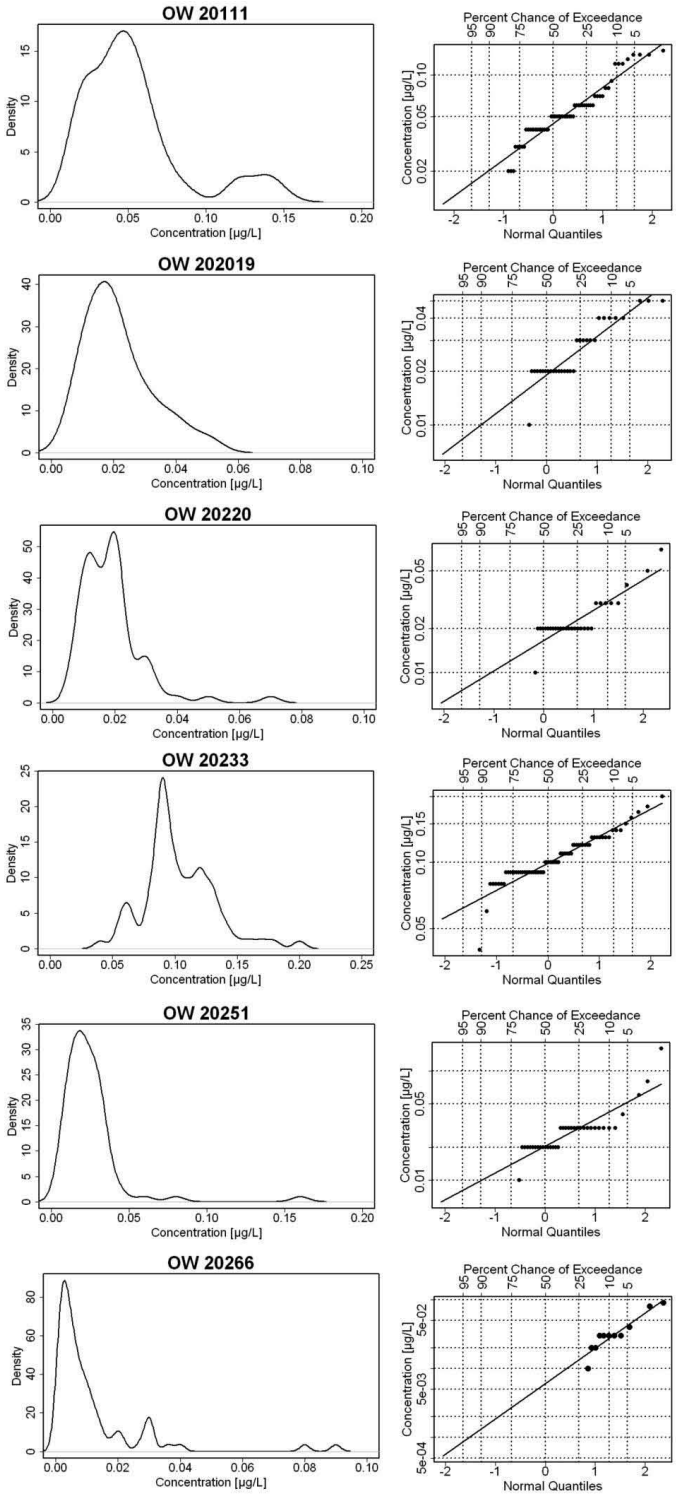

2006
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
2007
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
2008
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
2009
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
2010
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
2011
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles

Fig. 9d


OW 20111
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
OW 202019
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
OW 20220
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
OW 20233
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
OW 20251
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles
OW 20266
Density
Concentration [µg/L]
Percent Chance of Exceedance
Concentration [µg/L]
Normal Quantiles

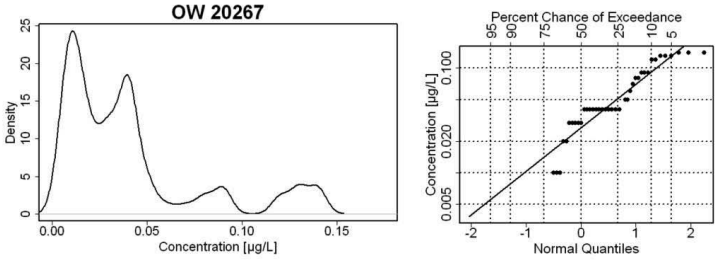


Figure 9: Left side: Kernal density distribution functions of atrazine concentration data (observed and modeled values for nonquantifiable values) for a) ROS application tests (see Table 3), b) years (1991/1992 to 2005), c) years (2006 to 2011), d) single observation wells. Right side: Probability plots with linear regressions using the plotting positions of the uncensored observations and their normal quantiles. These models are then used to estimate the concentration of the censored observations as a function of their normal quantiles.

Table 4: Linear model output parameters of linear regressions using uncensored observations and their normal quantiles for the estimation of nonquantifiable values. Superscripts indicate significant differences from zero using the t-test with
[a] α = 0.000, [b] α = 0.05, [c] α= 1 (nonsignificant difference from zero)

Dataset	Data transformation	Estimated coefficients		R^2
		Slope	Intercept	
Atrazine ROS (real LOQ)	log	1.28[a]±0.02	-3.47[a]±0.01	0.89
Atrazine ROS (LOQ: 0.05 µg L^{-1})	log	0.92[a]±0.01	-3.04[a]±0.01	0.97
Atrazine ROS (LOQ: 0.1 µg L^{-1})	log	0.81[a]±0.01	-2.88[a]±0.01	0.98
DEA ROS (real LOQ)	log	0.95[a]±0.02	-3.31[a]±0.04	0.88
DEA ROS (LOQ: 0.05 µg L^{-1})	log	0.93[a]±0.01	-3.29[a]±0.01	0.96
DEA ROS (LOQ: 0.1 µg L^{-1})	log	0.95[a]±0.02	-3.32[a]±0.04	0.88
1991/1992	log	1.63[c]±0.71	-4.91[b]±0.88	0.72

Dataset	Data transformation	Estimated coefficients		R^2
		Slope	Intercept	
2000	log	1.03[a]±0.08	-3.16[a]±0.08	0.93
2001	log	0.89[a]±0.12	-3.03[a]±0.11	0.92
2002	log	0.70[a]±0.07	-3.41[a]±0.07	0.94
2003	log	0.34[a]±0.07	-2.80[a]±0.07	0.70
2005	log	1.06[a]±0.05	-3.39[a]±0.05	0.86
2006	log	1.06[a]±0.05	-3.52[a]±0.03	0.88
2007	log	1.79[a]±0.05	-4.09[a]±0.04	0.93
2008	log	1.40[a]±0.03	-3.41[a]±0.02	0.95
2009	log	1.23[a]±0.06	-3.09[a]±0.06	0.83
2010	log	0.84[a]±0.02	-2.89[a]±0.02	0.94
2011	log	0.74[a]±0.02	-2.84[a]±0.02	0.93
Observation wells				
20111	log	0.61[a]±0.02	-3.11[a]±0.02	0.93
20219	log	0.50[a]±0.04	3.96[a]±0.04	0.85
20220	log	0.48[a]±0.05	-4.10[a]±0.05	0.77
20233	log	0.28[a]±0.01	-2.31[a]±0.01	0.89
20251	log	0.57[a]±0.05	-3.89[a]±0.04	0.78
20266	log	1.18[a]±0.15	-5.12[a]±0.23	0.87
20267	log	0.96[a]±0.06	-3.62[a]±0.05	0.89

Table 5: Number of samples, sampled observation wells and the fraction of nonquantifiable values for each year of groundwater monitoring of the Zwischenscholle aquifer.

Dataset	Number of samples	Number of observation wells	Fraction of nonquantifiable values
1991/1992	16	16	75%
2000	33	19	61%
2001	23	15	59%
2002	26	26	65%
2003	32	32	59%
2005	111	19	51%
2006	232	28	37%
2007	202	24	44%
2008	156	22	23%
2009	143	11	43%
2010	136	11	46%
2011	138	11	46%
Observation wells			
20111	74	-	19%
20219	69	-	55%
20220	73	-	60%
20233	76	-	9%
20251	74	-	51%
20266	74	-	85%!
20267	77	-	49%

4.1.4 Groundwater and triazine fluctuations in selected observation wells

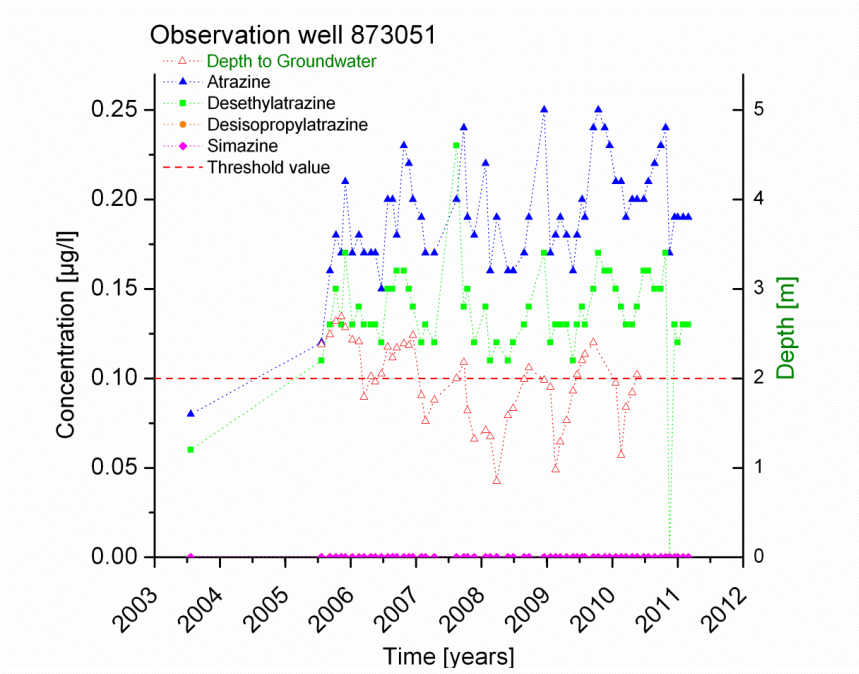
In this chapter, the trends and fluctuations of triazine concentrations in groundwater samples are analyzed with respect to groundwater level trends and fluctuations of the following observation wells:

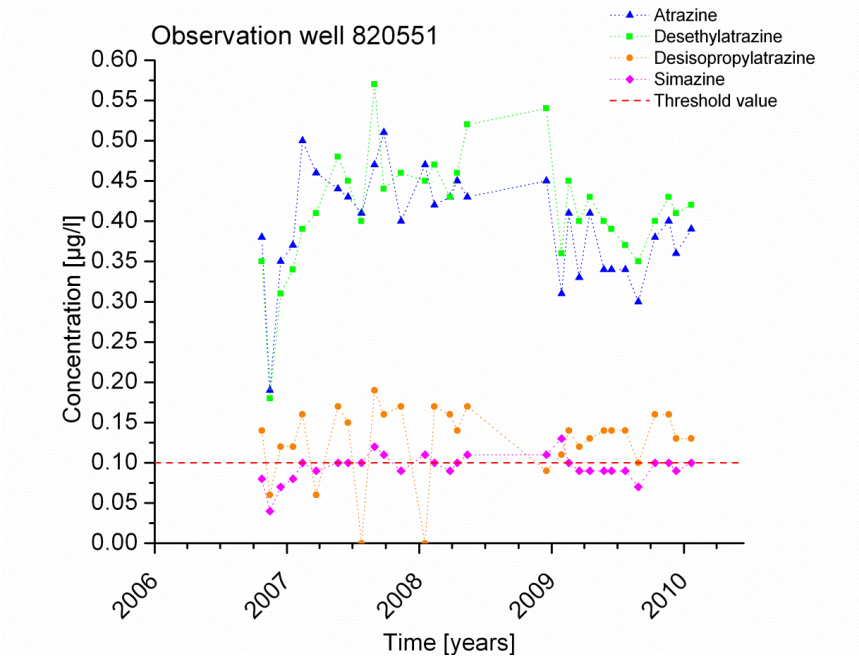
- OW 873051: Seasonal fluctuating triazine concentrations that correspond with fluctuations of the groundwater table are visible (Figure 10). Considering that the filter position (top of filter was 0.77 m below mean groundwater table, standard deviation of groundwater level (σ) = 0.61 m, filter length = 2.2 m) is within the groundwater fluctuation zone, atrazine concentrations seem to respond to groundwater fluctuation, i.e. showing a dilution effect. Whenever the water table rises, the pesticide concentration generally decreases. However, delays in atrazine concentration responses to groundwater fluctuation varying between 1 to 3 months comparing the corresponding peaks and dips were found.
- OW 1691: The filter top is 0.74 m above the mean groundwater table (σ = 0.50 m, filter length = 8 m). Similar to OW 873051, the filter is localized in the groundwater fluctuation zone and triazine dilution effects can be observed, again with partly delayed atrazine concentration responses.
- OW 20230: The filter top is 11.9 m below the mean groundwater table (σ = 0.6 m, filter length = 2 m), hence tapping groundwater in the lower part of the aquifer (aquifer bottom is 20 m below groundwater table). Atrazine concentration fluctuation in fact is visible, but doesn't correspond with groundwater fluctuation. Due to the fact that the analyzed groundwater samples were taken approximately 12 m below the mean groundwater table, the dilution effect of atrazine concentrations due to recharge from the unsaturated zone is highly deflated and delayed, dependent on vertical and lateral movement of groundwater. Conversely, this corroborates the hypothesis that dilution effects are more pronounced in the fluctuation zone, where the groundwater is in direct contact with the recharge from the unsaturated zone above.

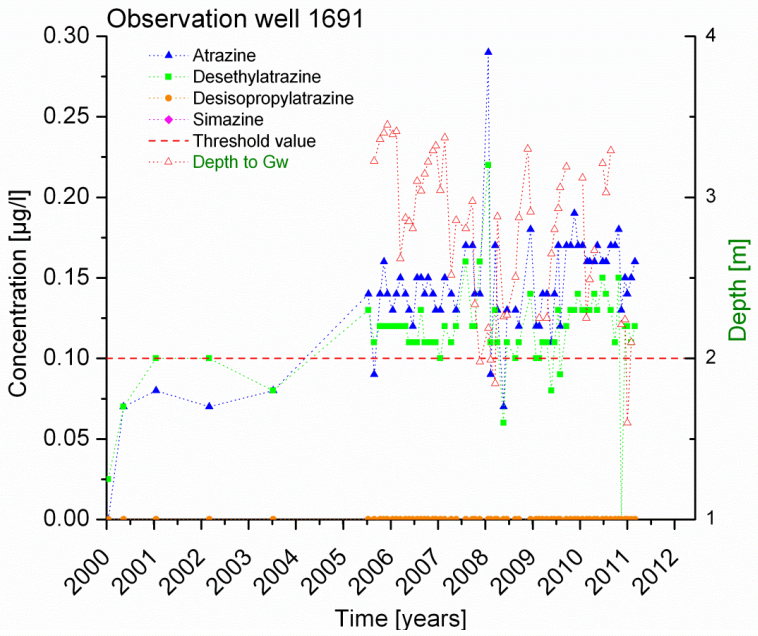
Because a large fraction of atrazine concentration peaks are delayed between 1 and 3 months with respect to groundwater fluctuation amplitudes (44% and 77% of the peaks for OWs 873051 and 1691, respectively) within time series of each individual OW, we obtained small correlation coefficients (873051: r = 0.09; 1691:r = 0.03) between groundwater levels and atrazine.

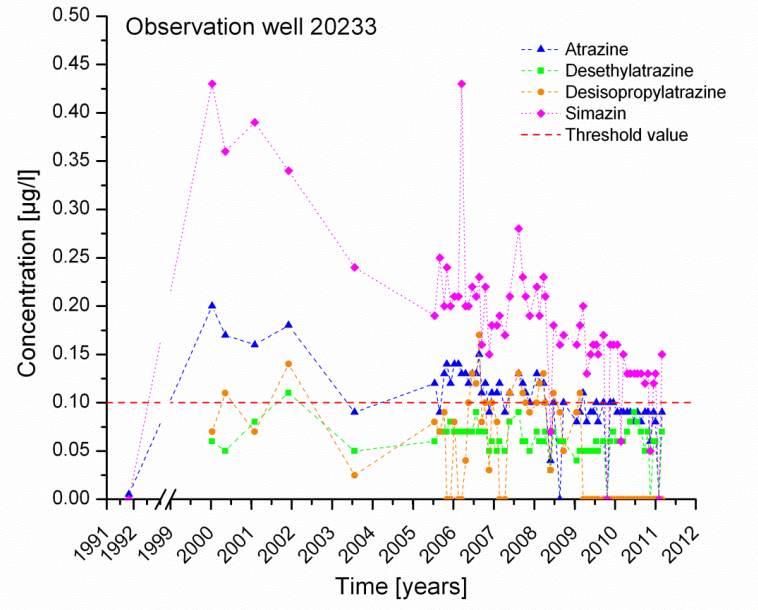
The dilution effect suggests that the recharge water contains less or no atrazine at all. Therefore, one might conclude that in the vadose zone in the immediate vicinity of respective OWs, there is no or negligible input of atrazine from the unsaturated zone into the aquifer.

When considering all OWs with a filter length smaller than 3 m, the filter depth with reference to groundwater table shows no distinctive correlation to atrazine concentration levels (Figure 11, page 75). This indicates that there is no consistent vertical gradient in atrazine concentrations in the aquifer. The spatial variation of the atrazine concentrations in the OW's in the Zwischenscholle aquifer should therefore be attributed to heterogeneous aquifer properties and spatial variations of atrazine source zones.


Observation well 873051
Depth to Groundwater
Atrazine
Desethylatrazine
Desisopropylatrazine
Simazine
Threshold value
Concentration [µg/l]
Depth [m]
Time [years]
0.00
0.05
0.10
0.15
0.20
0.25
0
1
2
3
4
5
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012


Observation well 820551
Atrazine
Desethylatrazine
Desisopropylatrazine
Simazine
Threshold value
Concentration [µg/l]
Time [years]
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
2006
2007
2008
2009
2010


Observation well 1691
Atrazine
Desethylatrazine
Desisopropylatrazine
Simazine
Threshold value
Depth to Gw
Concentration [µg/l]
Depth [m]
Time [years]
0.00
0.05
0.10
0.15
0.20
0.25
0.30
1
2
3
4
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012


Observation well 20233
Atrazine
Desethylatrazine
Desisopropylatrazine
Simazin
Threshold value
Concentration [µg/l]
Time [years]
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
1991
1992
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012

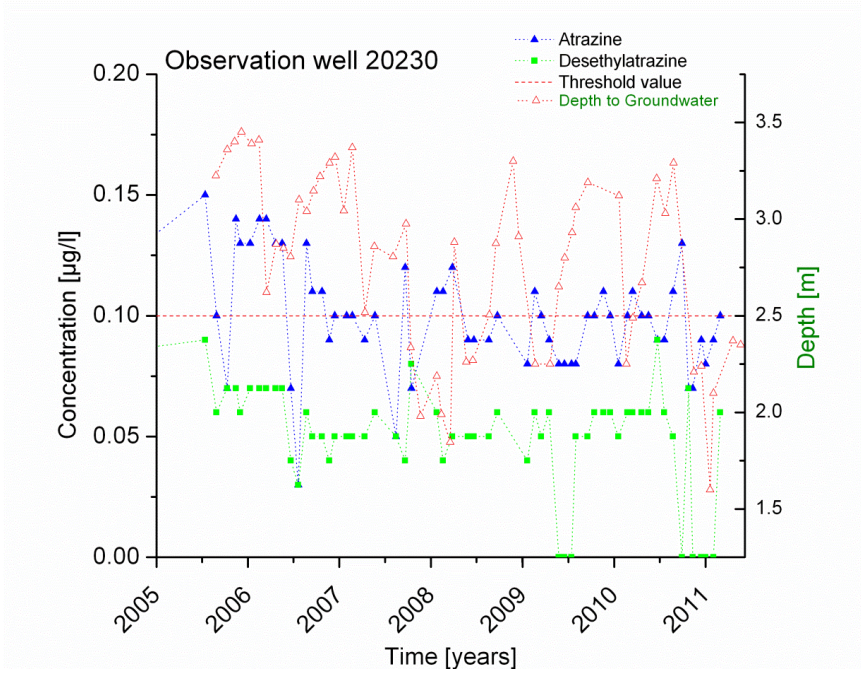


Figure 10: Time series of triazine concentrations and groundwater depths below the soil surface in 5 observation wells.

4.1.5 Deethylatrazine to atrazine ratio (DAR)

Thurman et al. (1998) found that with increasing atrazine concentration in groundwater samples of the Midwestern United States the deethylatrazine to atrazine ratio (DAR) decreased (Table 6). Accordingly high atrazine concentration levels were associated with point-source contamination. Similar to the findings of Thurman et al. (1998), the DARs of Zwischenscholle groundwater samples decrease with increasing atrazine concentration with the exception of OW 820551. OW 822951 with a mean atrazine concentration of 1.12 µg L^{-1} and a mean DAR of 0.02 can clearly be identified as point-source contamination. Additionally, this OW is located directly at a farmyard, where pesticide handling (e.g. transferring pesticides from tank to sprayers and washing sprayers) occurs. In the Zwischenscholle aquifer, atrazine concentrations mainly exceed those of DEA, resulting in a global DAR of 0.84. These findings are in line with those of Tesoriero et al. (2007) who found

atrazine concentrations generally exceeding those of DEA in environments with “thin” unsaturated zones, i.e. with water tables between 1 m and 8 m below land surface. Thus, the unsaturated zone of the Zwischenscholle study area with water tables ranging from 0.8 m to 7.3 m below land surface (Table 7) and an overall mean of about 4.9 m can be classified as mainly “thin”.

Figure 10 shows that constant DARs (OWs 1691, 820551), decreasing DARs (OW 873051), or increasing DARs with constant DEA- and decreasing atrazine concentration trends (OWs 20230, 20233) were observed. These findings are consistent with other groundwater monitoring studies after the ban of atrazine (Gutierrez and Baran, 2009, Tappe et al., 2002), in which different atrazine and DEA trends were observed in different monitoring wells in one catchment. Conversely, a typical behavior of atrazine and DEA concentration evolution after the last application was reported for surface waters: while DEA concentrations maintained on a constant level, atrazine concentrations decreased, resulting in an increasing DAR over time (Jabe, 2011, Ma and Spalding, 1997).

Table 8 shows mean DAR values in the Zwischenscholle Aquifer for each year. Smaller DAR values were observed in 91/92 close to the time of prohibition, and in 2000. Whether these smaller DAR values in 91/92 and 2000 compared to the years thereafter are related to ongoing metabolization of atrazine to DEA (increasing DAR) with time is difficult to conclude because of the limited number of available DARs and the considerable change in sampled OWs between the respective periods (e.g. Figure 5). The small DAR values in 1991/1992 are associated with low atrazine concentrations (max 0.09 µg L^{-1}, Figure 5) and a high fraction of nonquantifiable values (75%) so that these small DAR values are probably not related to point source contaminations which normally go along with high contamination levels as explained above. Relatively constant mean DARs in the years after 2000, especially in the years 2009 to 2011 when the same OWs were sampled, rather suggest an inert behavior of atrazine and its metabolites in groundwater. The overall Zwischenscholle long-term mean DAR of 0.84 indicates that atrazine mainly enters the aquifer in a diffusive way, i.e. via field application.

Table 6: Statistics of deethylatrazine to atrazine ratio (DAR) for the respective atrazine concentration ranges of i) Zwischenscholle sampling from 1991 to 2011 in comparison to i) according to values of the study of Thurman et al. (1998).

Range of atrazine concentration [µg L^{-1}]	Thurman et al. (1998)		Zwischenscholle 1991 - 2011			
	Median DAR	Number of Samples	Median DAR	Mean DAR	Number of Samples	
0.01 to 0.05	-	-	1.00	0.99	233	
0.05 to 0.1	1.8	61	0.86	0.79	203	
0.1 to 0.2	0.58	14	0.73	0.70	221	
0.2 to 0.4	0.6	14	0.70	0.80	48	
0.4 to 0.8	0.23	12	1.05	1.04	17	only 820551
0.8 to 2.1	0.23	9	0.02	0.02	29	only 822951

Table 7: Groundwater levels in observation wells (measured since 2005) and mean deethylatrazine-to-atrazine ratio (DAR).

OW	Count	Depth to groundwater table [m]				Mean DAR
		Mean	Min	Max	Standard deviation	
1691	61	2.8	1.6	3.5	0.5	0.84
20111	62	5.2	3.9	6.3	0.6	1.17
20219	63	3.2	2.7	5.7	0.4	0.76
20220	63	4.2	2.2	4.4	0.3	0.73
20230	63	4.8	2.5	5.8	0.6	0.55
20233	62	4.0	2.5	5.1	0.6	0.6
20251	65	4.1	1.1	5.1	0.9	1.2
20266	65	3.5	1.7	4.3	0.4	0.76
20267	63	6.4	4.3	7.3	0.6	0.78
820551	1	3.8	3.8	3.8	-	1.05
873011	64	2.1	1.0	3.0	0.5	1.00
873051	62	2.0	0.9	5.0	0.6	0.74

Table 8: Mean DAR values for each year.

Years	Mean DAR	Standard deviation of DAR	Number of DAR calculations
1991/1992	0.07	0.12	4
2000	0.38	0.32	10
2001	0.90	0.40	5
2002	0.79	0.55	7
2003	0.76	0.27	12
2005	0.77	0.42	64
2006	0.88	0.52	146
2007	0.98	0.55	114
2008	0.85	0.47	109
2009	0.78	0.32	81
2010	0.77	0.33	48
2011	0.76	0.38	62

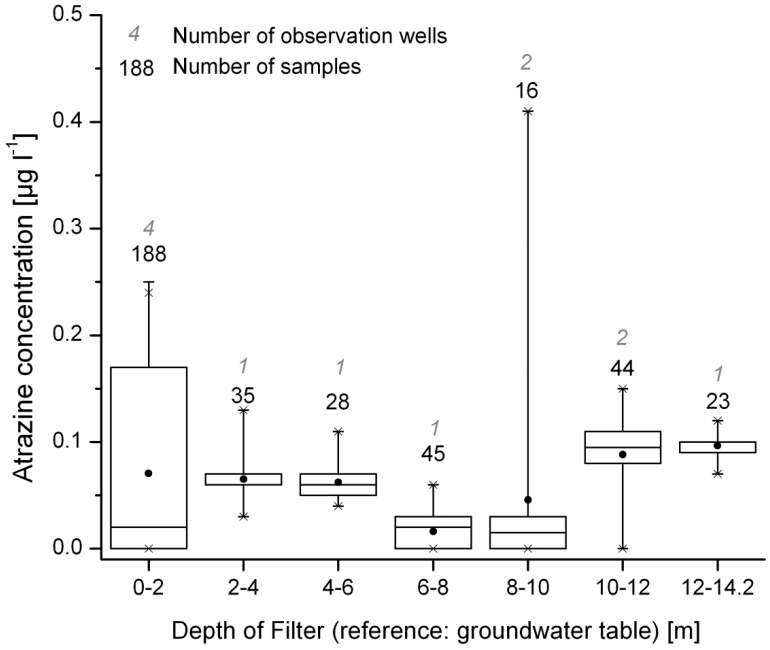


Figure 11: Boxplots of atrazine concentrations of all years for different depths of the upper boundary of the filter screen below the groundwater level. Only observation wells with a filter screen length of ≤ 3 m are considered here.

4.1.6 Principal Component Analysis (PCA)

Only the few first principle components which explain a large fraction of dataset variance are kept for interpretation (Table 9). In many studies only PCs are kept either with eigenvalues > 1 or explaining in total at least 60 to 70 percent of the data variance, but a standardized criterion for selecting meaningful PCs does not exist (Olsen et al., 2012). Accordingly “sensitivity analysis”, i.e. testing various PCA runs with and without respective variables and afterwards deciding which variables are kept is one appropriate approach. Rotation methods of principle components like “Varimax”, where variable loadings can be contributed more easily to particular principle components, were not deemed necessary for interpretation here and hence not applied.

The PC scores for the first two principle components were plotted together with - and hence scaled to - variable loadings (Figure 13). The scores of the 1st quadrant refer to OWs where atrazine and deethylatrazine were detected along with similar trends in nitrate concentration (mainly 1691 and 873051, 873011, 20111, 20267). The scores in the 4th quadrant are exclusively associated with OWs 20233 and 20230, where simazine and DIA are frequently detected besides atrazine and DEA. In the 2nd and 3rd quadrants the scores of OWs with large fractions of nonquantifiable values or low concentration levels are located (e.g. 20219, 20220, 20266 etc.), where low atrazine correspond to low nitrate concentration levels.

The variable loading vectors in the PCA plot (Figure 13) show a correlation between nitrate, EC, atrazine and DEA in one direction. Atrazine may be predominantly a nonpoint-source pollutant due to field application and subsequent leaching to the groundwater. The mean DAR value of 0.84 of the groundwater samples indicates nonpoint-source contamination of the Zwischenscholle aquifer. This is corroborated by the correlation between atrazine and nitrate which may also be related to leaching from intensively used agricultural fields. The distinct correlation might also be explained by similarities in trend and seasonal fluctuation of nitrate and triazine concentrations (Figure 12, OW 873051). A higher specific electrical conductivity in groundwater is also associated with widespread agricultural impact and is thus correlated with the occurrence of the previously mentioned compounds. The variable vectors of simazine, DIA and diuron are correlated in the same direction, showing negative loadings to PC2, but positive loadings – similar like atrazine and DEA – to PC1. DIA can be a metabolite of either simazine or atrazine and since Figure 10 shows only DIA detects in the presence of simazine detects, the correlation between DIA and simazine is clearly visible in the PCA. Simazine and hence DIA detects are limited to a few OWs and therefore independent of atrazine and DEA findings. The correlation of diuron and simazine might be due to the use of a mixed pesticide product containing both compounds (e.g. Simazole plus, Makhteshim Agan Industries).

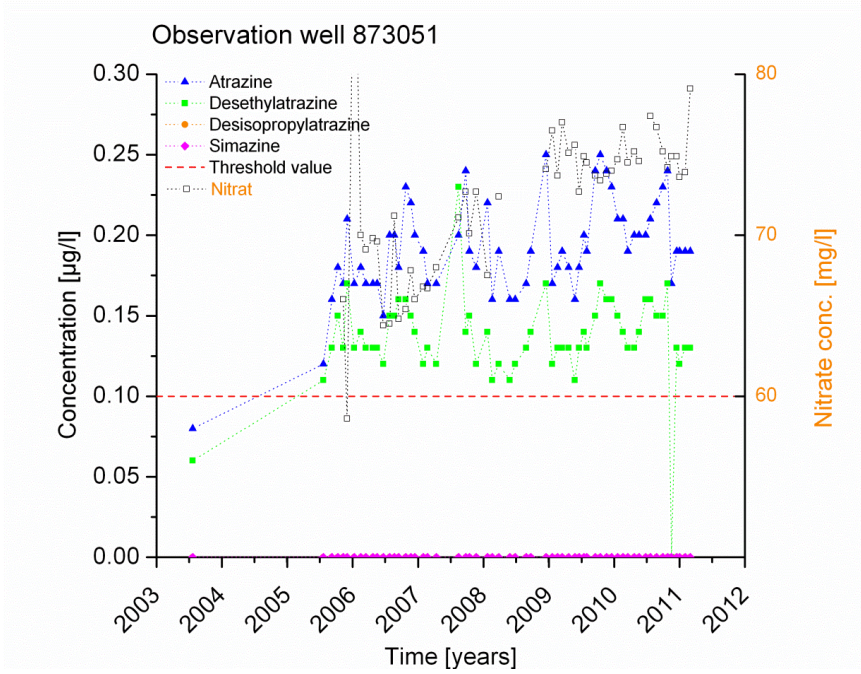


Figure 12: Triazine and nitrate concentrations of groundwater samples for observation well 873051.

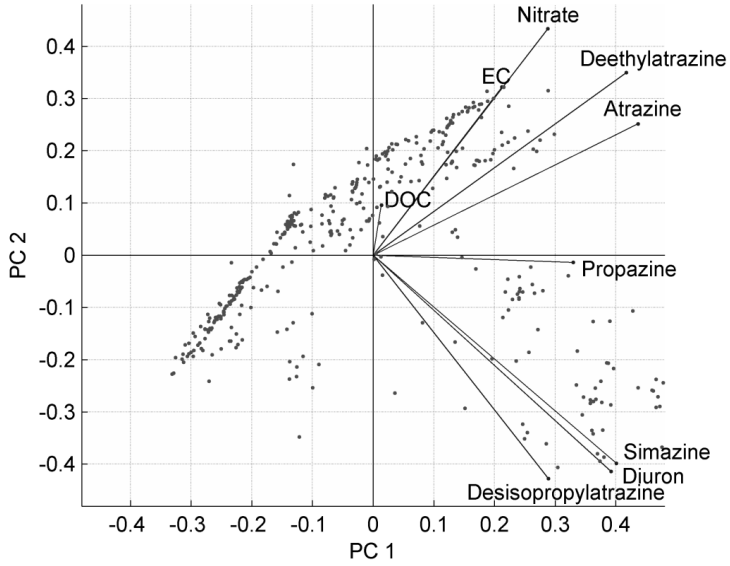


Figure 13: Loadings and scores plot of PCA.

Table 9: Statistical parameters of PCA results.

Principle Component	Percent explained [%]	Percent explained – cumulative [%]	Eigenvalues
1	35.15	35.15	3.16
2	24.29	59.44	2.19
3	12.96	72.40	1.16
4	10.93	83.33	0.98

4.2 Soil residue analysis

4.2.1 Soil parameters

Soil parameters are presented in Table 10. Considering that the percentage of fine fraction (≤ 2 mm) is highly variable with depth between the soil cores (KS-A-1-3, Table 11), with an overall decreasing trend of the fine fraction with depth, variation of total sorption capacity in space needs to be considered accordingly. The organic carbon content is highest with 1.35 % by weight in the topsoil and decreases strongly below a depth of 30 cm. The effective CEC is relatively stable down to a depth of 200 cm and then decreases. Slightly varying pH values with a mean of 6.6 indicate more neutral to marginal acidic conditions. Since atrazine is a weak base (pk_a of 1.7), protonation of atrazine at reported pH values is negligible and hence is not affecting the sorption behavior.

Table 10: Soil parameters and grain size distribution of all layers from soil core KS-A-3.

Depth [cm]	Sand[1] (%)	Silt[2] (%)	Clay[3] (%)	pH	Effective CEC (meq/100g)	Organic Carbon (%)
0-10	49.6	45.5	4.9	6.8	11.4	1.35
10-30	63.4	32.8	3.8	6.7	11.1	1.22
30-60	63.6	32.9	3.5	6.6	10.0	0.62
60-100	66.3	31.3	2.4	6.7	13.5	0.23
100-150	72.9	25.4	1.7	6.8	11.4	0.11
150-200	58.3	38.3	3.4	6.7	11.0	0.05
200-250	66.4	29.9	3.7	6.4	7.2	0.05
250-300	76.0	20.5	3.5	6.3	6.3	0.08

[1]2000-63 µm
[2]63-2 µm
[3]<2 µm

Table 11: Fraction of fine soil (< 2 mm) from total soil.

Depth (cm)	Fine fraction, < 2 mm (%)		
	KS-A-1	KS-A-2	KS-A-3
0-10	97.0	98.0	99.1
10-30	92.7	99.0	98.0
30-60	68.6	99.2	99.5
60-100	28.1	99.3	99.3
100-150	21.9	49.5	99.4
150-200	30.8	27.0	89.7
200-250	30.5	27.9	73.6
250-300	23.2	31.3	57.7

4.2.2 Accelerated Solvent Extraction (ASE) method validation

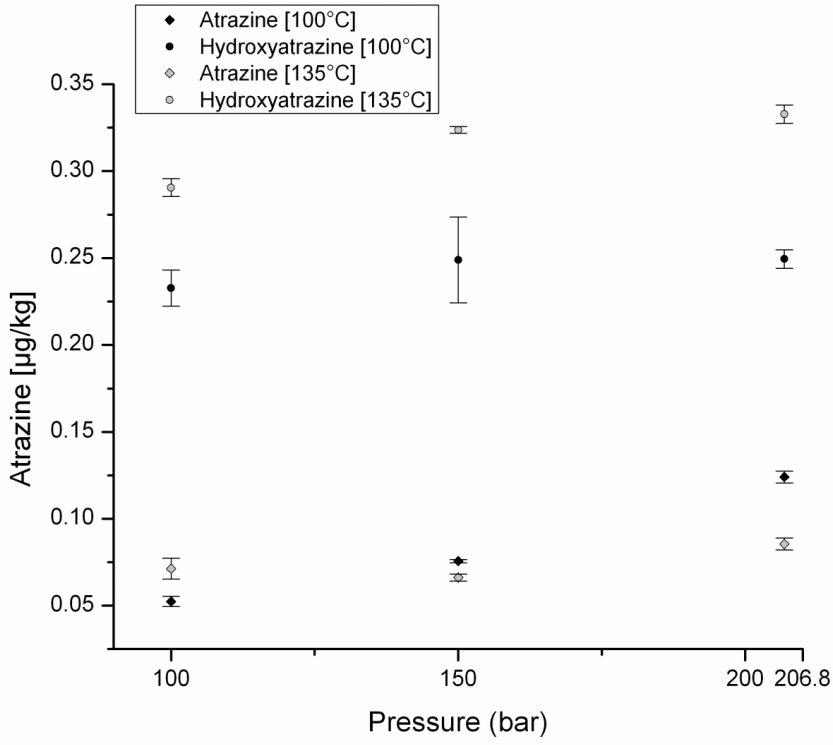


Figure 14: Extraction yields of Krauthausen soil B (KS-B) for different ASE temperature - pressure combinations. Error bars indicate standard deviations for triplicates.

The results of the method validation are presented in (Figure 14). Atrazine yields are generally higher for higher pressures. Possibly the higher pressure facilitates soil matrix penetration by the solvent. Furthermore the solvent remains in the liquid phase at high temperatures and high-pressures. The highest atrazine concentration was obtained extracting with 100°C and 207 bar, whereas for 135°C at the same pressure the concentration was 31 % lower. Chromatograms of LC-MS/MS-Analysis (Appendix B: Figure 16, Figure 17) for the extracts using 100°C and 207 bar show atrazine peaks with a higher signal-to-noise ratio (20.8:1; atrazine peak height: 1250; background height: 60) and a higher atrazine peak area (5549; background area: 60) compared to extracts using 135°C and 207

bar (signal-to-noise ratio: 10.8:1; atrazine peak height: 650; background height: 200; atrazine peak area: 3920; background area: 60). Probably, the higher extraction temperature lead to an increased co-extraction of soil-matrix compounds, which caused a quenching effect and hence a reduction of atrazine peak area and height. Furthermore, the higher extraction temperature of 135°C could possibly cause a partial decomposition of the analyte, in particular under the high extraction pressure of 207 bar, in contrast to 100°C. Supporting information and chromatograms of LC-MS/MS analysis can be found in the Appendix B: (Figure 16, Figure 17). In comparison, the parameter setup of 135°C and 100 bar for atrazine residue extractions used by e.g. Jablonowski et al. (2009) and Martinazzo et al. (2010), yielded 43% less than those obtained by 100°C and 207 bar.

For 2-hydroxyatrazine all extractions conducted with 135°C yielded higher concentrations. Because the main focus was on atrazine in this study, the optimized method with regard to the highest atrazine yield (100°C, 207 bar) was selected for soil core sample extractions.

4.2.3 Triazine extraction recoveries

Extraction recoveries of atrazine were 103 % and 108 % for 0.1 μg kg^{-1} and 1.0 μg kg^{-1}, respectively. For 2-hydroxyatrazine recoveries were 91.3 % and 98.0 % for 0.1 μg kg^{-1} and 1.0 μg kg^{-1}, respectively. Standard deviations of triplicates range between 4 % and 9 %. This extraction recovery test can only indicate the general efficiency of recovery using the accelerated solvent extraction technique with respect to soil samples which were freshly spiked with atrazine and 2-hydroxyatrazine. Accordingly, the extraction recovery for soil samples with aged atrazine and 2-hydroxyatrazine is unknown, but probably smaller due to larger fractions of the triazines being adsorbed more strongly (covalent bonds) and/or being entrapped in the soil matrix (cp. Chapter 1.1.3).

Although atrazine was never applied for weed control in SeS samples, it could be detected together with 2-hydroxyatrazine at concentrations of 0.065 μg kg^{-1} and 0.033 μg kg^{-1} with standard deviations of 2 %, respectively. This findings can be explained by shift

contamination or contamination via atmospheric deposition as found e.g. in Europe or North of America (Bossi et al., 2002, Brun et al., 2008). Thus an atrazine background contamination of land surfaces needs to be considered generally.

4.2.4 Triazine residues in soil cores

The results of atrazine and 2-hydroxyatrazine soil extracted concentrations are presented in Figure 15 (page 88). Atrazine concentrations are highest in the top soil layers (ranging between 0.15 μg kg^{-1} and 0.2 μg kg^{-1}) and decreasing subsequently with depth (ranging between 0.01 μg kg^{-1} and 0.02 μg kg^{-1} in the lowermost layer). However, for the top soil layer atrazine concentrations are only 2.3 to 3 times higher than those of SeS samples, which may reflect background contamination in this area. Below a depth of 30 cm atrazine concentrations as well as the organic carbon content sharply decrease, whereas 2-hydroxyatrazine concentrations do not decrease as strongly as atrazine concentrations do, which is an indication for the higher sorption potential of 2-hydroxyatrazine in soils and particular to the clay fraction, as already found by Vryzas et al. (2007), Lerch et al. (1998) and Winkelmann et Klaine (1991). Triazine residue concentrations are variable within one field of 1.98 ha as indicated by the coefficients of variation, which vary between 0.07 and 0.36 and between 0.24 and 0.65 for atrazine and 2-hydroxyatrazine, respectively (Table 12, page 89). The variability in 2-hydroxyatrazine concentrations is higher than that of atrazine, especially due to soil core KS-A-1, which contains much lower 2-hydroxyatrazine concentrations in most cases (partly > 50 % down to 30 cm) compared to KS-A-2 and -3. Conversely, KS-A-1 atrazine concentrations are either within the range of KS-A-2 and -3 or even higher. This might be due to locally varying degradation capacity or sorption behavior and hence varying physico-chemical and microbiological soil properties.

Based on Equation 2 and assuming three single atrazine applications with a recommended dose of 0.96 kg ha^{-1} averaged residual atrazine accounts for 0.01 % of the applied mass in the top layer and 0.07 % in the total soil profile.

$$RS\ [\%] = \frac{\sum_i^n AC_i[\mu g\ kg^{-1}] \times \rho\ [kg\ m^{-3}] \times A\ [m^2] \times t_i\ [m]}{AAM\ [\mu g]} \times 100\ [\%] \qquad \textbf{Equation 2}$$

RS is the residual atrazine, AC_i is the averaged atrazine concentration of the i-th layer (i = 0 – 0.1 m,…, n = 2.5 – 3.5 m, see Table 11, page 80 for layer information) of all 3 Krauthausen soil cores, ρ is the soil bulk density (1500 kg m^{-3}), A is the area (1,98 ha or 19800 m^2), t_i is the thickness of the i-th layer and AAM is the total applied atrazine mass in the area A. However, these are approximate estimates, because spatial information of atrazine field applications and the correct number of applications (2 or 3 times) are not available. Compared to our findings Jablonowski et al. (2009) found slightly higher percentages of residual atrazine (0.03 % or 1.00 μg kg^{-1}) in the topsoil layer of an outdoor lysimeter 22 years after the last application. For this lysimeter, 25 % of the initially applied ^{14}C-activity was still present after more than two decades and in the top layer (0-10 cm) 60 % of this residual ^{14}C (bound-and extractable residues and fragments of mineralized ^{14}C-atrazine incorporated into the soil matrix) was extractable. Extracted atrazine accounted for 0.35 % of residual ^{14}C. This information suggests that i) a high portion of initially applied atrazine most probably degraded, ii) an unknown portion of the 40% non-extractable ^{14}C may be associated with atrazine and its metabolites and iii) also in our study unknown but possibly distinctive fractions of non-extractable atrazine and metabolites need to be considered. Latter conclusion hints at the fact that the atrazine recovery for aged atrazine residues is lower compared to freshly spiked atrazine soil samples, as already suggested in chapters 3.2.5 and 4.2.3. Affirming this, Loiseau and Barriuso (2002) found that up to 50% of bound residues were associated with atrazine itself and its main metabolites in the organic C rich soil size fraction < 20 μm, suggesting that generally total atrazine residue concentrations might be distinctively higher than extractable atrazine concentrations.

Long-term leaching of both extractable and non-extractable pesticide residues facilitated by microbial activity (Khan and Behki, 1990), dry-wet cycles (Jablonowski et al., 2012a,

Pignatello and Ferrandino, 1993) especially under changing environmental conditions, earthworm activity (Gevao et al., 2001) and other factors like change in agricultural practices and introduction of chemicals which are able to change chemical properties of the soil (Gevao et al., 2000) might be possible.

A simplified calculation using Equation 3, based on averaged atrazine concentrations for each layer of the 3 Krauthausen soil cores (AC_i) leads to a total mass of atrazine residues of 3674 mg (1856 mg ha^{-1}) for the entire Krauthausen field (KS-A) with an area (A) of 1.98 ha,

$$ARM\ [mg] = \sum_{i}^{n} AC_i\ [mg\ kg^{-1}] \times \rho\ [\ kg\ m^{-3}]\ x\ A\ [m^2]\ x\ t_i\ [m] \qquad \textbf{Equation 3}$$

where ARM is the atrazine residues mass, AC_i is the averaged atrazine concentration of the i-th layer (i = 0 – 0.1 m,…, n = 2.5 – 3.5 m) of all 3 Krauthausen soil cores, ρ is the soil bulk density (1500 kg m^{-3}), A is the area (1.98 ha or 19800 m^2) and t_i is the thickness of the i-th layer. For the entire Zwischenscholle aquifer, atrazine groundwater concentration would raise by 0.002 µg L^{-1} due to Equation 4, if the investigated field would be representative for all fields in the Zwischenscholle area where atrazine was applied and if all atrazine residues would be leached out instantaneously and mixed with the entire groundwater body (considering the Zwischenscholle study area of 21 km^2 (TA) a potential atrazine soil residue area ($ASRA$) of 0.56 km^2or 56 ha according to 4 % maize of total agricultural area (2.8% of total area) (Mouvet et al., 2004), a mean aquifer thickness (t) of 10.9 m (Jahn, 2002), an effective porosity (θ) of 0.25 (Lahmeyer, 1984) and a mean atrazine residue mass (ARM) of 1856 mg ha^{-1} in treated fields).

$$GWAC\ [\mu g\ L^{-1}] = \frac{ARM\ [mg\ ha^{-1}] \times ASRA\ [ha]}{TA\ [m^2] \times t\ [\mathrm{m}] \times\ \theta} \qquad \textbf{Equation 4}$$

Since an instantaneous desorption and release of all extractable and non-extractable atrazine residues is highly unlikely, this estimate of concentration raise must be considered as (overly) conservative. Conversely, dissipation via plant uptake (Dec et al., 1997), uptake by earthworms (Fuhremann and Lichtenstein, 1978), microbial degradation of bioavailable fractions of (aged) atrazine residues (Barriuso et al., 2004) needs to be accounted for. Furthermore the upward movement of groundwater with higher atrazine concentrations can result in an increase of atrazine sorption on to subsoil material. Another uncertainty is the distribution of atrazine residue concentrations on the macro scale which might vary within one field as indicated by our findings and also between the different fields of the Zwischenscholle region which potentially have an atrazine application history but are not known. Hence, this calculation only gives a hint about remaining possible atrazine inputs from the vadose zone to groundwater 21 years after the ban of atrazine.

Based on this scenario, long term leaching of aged atrazine residues from the vadose zone seems to marginally contribute to sustaining average groundwater concentrations of the Zwischenscholle aquifer, which remained constantly close to the threshold limit of 0.1 µg L^{-1} even 20 years after the ban of atrazine (Vonberg et al., 2014). However, with regard to a high spatial variability in atrazine groundwater concentrations in the Zwischenscholle aquifer, as found in the latter study, ongoing local leaching of atrazine from soil residues might result in locally elevated atrazine groundwater concentrations. This becomes obvious considering the release of all atrazine residues of an area of 1 ha (1856 mg), transport to and instantaneous mixing with the groundwater below (using Equation 4 and substituting the Zwischenscholle test area TA by an area of 1 hectare), resulting in a local atrazine groundwater concentration of 0.068 µg L^{-1}. Multiplying that concentration of 0.068 µg L^{-1} by 0.028 (2.8% potential atrazine residue area of total study area) results in an atrazine concentration of 0.002 µg L^{-1} for the entire groundwater body of the Zwischenscholle study area, as already given above. Again, this calculation is simplified and should be treated as conservative estimate. To put the conservativeness of this calculation in perspective, using a

similar approach to calculate the risk of groundwater contamination for an applied dose of 0.96 kg ha^{-1} (i.e. assuming instantaneous leaching and mixing with the aquifer body without any decay) would lead to a groundwater concentration of 35.2 µg L^{-1}. Generally, leaching of soil adsorbed atrazine over time contributing to elevated atrazine groundwater concentrations need to be considered and assessed. This is particularly relevant in cases of atrazine threshold exceedances in groundwater years after its ban, like reported e.g. by Vonberg et al., (2014) or chapter 4.1. of this study, respectively and Vryzas et al., (2012c), who found atrazine concentrations in groundwater above the regulatory threshold of 0.1 µg L^{-1} in 42 % of all groundwater samples of aquifers of North-eastern Greece.

Considering averaged extracted atrazine concentrations of the three soil cores (KS-A-1 to 3) and assuming 3 applications of 0.96 kg atrazine per hectare 21 years ago, atrazine – in case of first order or exponential decay (Equation 5) – has approximately a half-life of 2 years within the unsaturated zone of the Krauthausen soil A.

$$T_{\frac{1}{2}} = \frac{\ln 2}{\ln(\frac{N_0}{N})} t \qquad \textbf{Equation 5}$$

$T_{\frac{1}{2}}$ = half-life value, N_0 = initial quantity of atrazine, N = measured quantity of atrazine after time t

The atrazine half-life of approximately 2 years only can be taken as rough estimate and most probably underestimates the atrazine half-life time in this soil, because i) non-extractable atrazine could not be included in the calculation and ii) the first two applications were executed before 1991 (information of the exact time of application is missing). Conversely, when adsorbed to soil on the long-term accompanied by an increasing resistance to biodegradation (Hatzinger and Alexander, 1995, Pignatello and Xing, 1996, Scribner et al., 1992), atrazine first-order decay in soils is less likely, whereas a multi-rate decay might be appropriate. Calculating half-lives of experimental data assuming first-order decay, whereas multi-rate processes are rather likely, could result in an overestimation of decay rates,

especially for long-term experiments. However, despite of these uncertainties these findings show that atrazine persistence in the field might be longer than predicted assuming first-order degradation dynamics using half-life values obtained from lab experiments which reach a maximum of 433 days (1.19 years) for topsoils as reviewed in chapter 1. Our findings are in line with those of Jablonowski et al., (2012b), who demonstrated that apparent half-lives of various pesticides in long-term outdoor studies exceeded by far those found in literature, which are mainly based on short-term experiments. This indicates that the environmental behavior of atrazine (and metabolites) and other pesticides similar in nature need to be re-considered for risk assessment and regulation procedures as already suggested by Jablonowski et al., (2011). Furthermore monitoring of these compounds in groundwater and soils is still inevitable even after two decades of its ban.

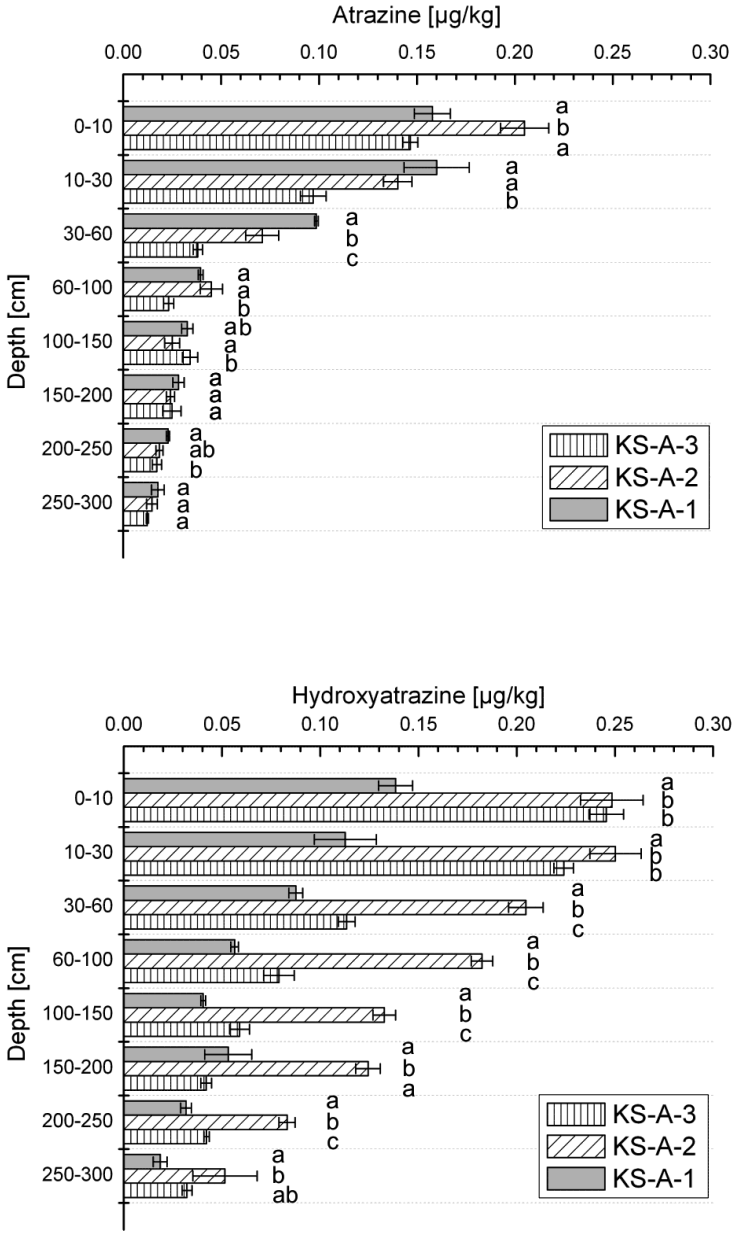


Figure 15: Concentration profiles of atrazine and 2-hydroxyatrazine residues determined by three soil cores (KS-A-1 to 3) of the Krauthausen gleyic cambisol, 21 years after the ban of atrazine. Error bars show standard deviations of triplicates. Different letters indicate significant differences of mean atrazine concentrations between Krauthausen soil profiles for $p < 0.05$, using the Tukey test.

Table 12: Coefficient of Variation for atrazine and 2-hydroxyatrazine concentrations is presented for the respective layers of the Krauthausen soil cores.

Depth [cm]	Coefficient of Variation	
	Atrazine	2-OH-Atrazine
0-10	0.15	0.24
10-30	0.20	0.30
30-60	0.36	0.37
60-100	0.26	0.52
100-150	0.13	0.52
150-200	0.07	0.50
200-250	0.12	0.42
250-300	0.15	0.65

5. Highlights and Conclusions

5.1 Atrazine groundwater monitoring

The results of long-term macro-scale atrazine monitoring demonstrate that the atrazine concentrations vary considerably in space in the aquifer but that the spatial pattern of the concentration distribution is relatively stable over the 20 years of monitoring period. This highly heterogeneous atrazine concentration distribution might be related to aquifer heterogeneity and spatial variation of source zones. A complete and accurate overview of pollutant concentration distribution of the entire aquifer is thus difficult to obtain. Additionally, a changing selection of observation wells over time with a tendency to sample those OWs with clearly detectable atrazine concentrations more frequently, results in statistics of sampled OWs which may not be representative for the entire aquifer. Optimizing descriptive statistics using data censoring techniques might hence not necessarily produce a more realistic estimation of groundwater contamination, but rather improve the precision of summarizing statistics of the dataset. In contrast, descriptive statistics using data censoring like “ROS” applied to each well separately can provide more realistic values for local atrazine contamination. Thus it is difficult to estimate, if atrazine concentrations remain on a constant high level for the entire Zwischenscholle aquifer like suggested by the monitored wells, while partially excluding OWs with negligible contaminant findings over time. For single OWs decreasing, constant and even upward atrazine concentration trends lasting until today were observed. Different processes may contribute to these concentration evolutions:

- The atrazine degradation potential in this aquifer seems negligible and consequently concentrations might only be diluted slowly due to a large groundwater volume compared to the groundwater recharge.
- Due to a high persistence of atrazine in the unsaturated zone and a potential of subsequent release, there might be atrazine stocks in the vadose zone. Gradual desorption and leaching represents a possible source of atrazine input to

groundwater. However, lower atrazine concentrations accompanied by higher groundwater levels rather suggest local dilution by water leaching from the vadose zone. The changes of atrazine concentrations due to this dilution occur within a relatively short time period when compared with the overall residence time of the groundwater in the aquifer. In order to relate the short time dynamics and the long term evolution of groundwater concentrations, lateral mixing processes in the aquifer need to be understood.

Concluding, these findings point at the general challenge to estimate mean concentrations of contamination for entire aquifers and thus it might be often questionable if threshold values are exceeded or not. Because regulation procedures are based on threshold values, the question of threshold exceedance is fundamental and needs to be answered clearly with as little uncertainty as possible. For single OWs monitoring local aquifer contamination this question can be answered clearly, but for an entire aquifer it may remain uncertain, if a monitoring system provides representative information of macro scale contamination.

The high persistence of atrazine concentrations in a number of observation wells over a long time after its presumed stop of application also raises questions about the use of groundwater monitoring studies as a strategy to evaluate the safe use of pesticides. The slow reaction of groundwater quality parameters after a changing pesticide application also applies for the change in groundwater concentrations after a new substance has been introduced.

5.2 Atrazine soil residue analysis

In this study, it was found that atrazine and 2-hydroxyatrazine residue concentrations can be detected in a field soil more than 21 years after the last application of atrazine. The residue concentrations vary distinctively within one field, whereas the concentration profiles of atrazine and 2-hydroxyatrazine show similar trends in the three investigated soil profiles with higher concentrations in the organic rich top soil decreasing continuously with depth.

Atrazine concentrations decreased sharply below a depth of 30-60 cm, whereas for 2-hydroxyatrazine the concentration decreased less with depth, what could be explained by the higher sorption capacity of 2-hydroxyatrazine compared to atrazine, especially to clay minerals. Atrazine residue concentrations in the topsoil of a field that received atrazine more than 21 years ago were only 2.3 to 3 times higher than in soil, were atrazine was never applied, suggesting a significant atrazine background contamination. Based on found atrazine concentrations (ranging between 0.2 $\mu g\ kg^{-1}$ and 0.01 $\mu g\ kg^{-1}$ for topsoil and subsoil, respectively), and considering the small fraction of the area in the region where atrazine was applied, long-term leaching could not sustain averaged concentrations of atrazine in the entire aquifer on a high level. But a local increase of atrazine groundwater concentrations due to leaching from the vadose zone might be possible.

The atrazine residence time in a field soil might be distinctively higher than suggested by the highest lab-derived half-life values found in literature. This result points at the difficulty of evaluating residence times and leaching potentials of (aged) atrazine residues in the vadose zone and the effect on atrazine groundwater concentrations on the long term.

Accordingly the environmental behavior of atrazine, its metabolites and generally pollutants with similar physico-chemical properties needs to be re-considered for risk assessment and regulation procedures. Therefore monitoring of these compounds in groundwater and field soils is essential even two decades after their ban.

The investigated fields and the study area do not represent fields and areas with a long history of high atrazine applications. Since even under these conditions detectable atrazine residues in soils and groundwater could be observed, more research is needed for an accurate assessment of long-term atrazine leaching, especially for fields with a prolonged atrazine application history and thus higher quantities of atrazine residues.

5.3 Perspective on the long-term fate of atrazine in soils and model predictions

The fate of a chemical in the environment is dependent on many environmental influences and can be characterized mainly by sorption and degradation. These mechanisms can be quantified and expressed as parameter values, the organic carbon normalized distribution coefficient (K_{OC}) or sorption coefficient K_d, and $t_{d,50}$ (time required for the total amount of a chemical at time of application to decline to 50 %) or dissipation half-life, for which the amount of a chemical subsequently continues to decline by 50 % for the same time interval. Models for simulations of pesticide fate in the environment like MACRO (Jarvis, 1994, Larsbo and Jarvis, 2003), which is the most widespread model for research and management purposes like pesticide registration (Mouvet et al., 2004), are based on those parameter values. There, dissipation of pesticides in soils is described by exponential functions conforming to first-order kinetics. Because model simulations are highly sensitive to degradation parameter values, it is thus essential that precise values, their variability in space, both horizontally and vertically, and information about their uncertainty need to be known for reliable model outcomes. Accordingly, catchment-scale pedotransfer functions implemented into those models need to be based on proper understanding of spatial variable herbicide retention and degradation and how they are affected by soil properties and environmental influences on the catchment scale. Until now there is a lack of the understanding of how herbicide degradation rates vary according to spatial heterogeneity and important determining factors influencing degradation like microbial ecology and its spatial variability have been neglected so far (Charnay et al., 2005).

Numerous laboratory and field studies on the fate of atrazine in the environment have been published, with highly varying results. Thus, the classification of the persistence of atrazine in the soil environment is a controversy, ranging between non-persistent (PPDB, 2013), and highly persistent as found for aged atrazine residues (Jablonowski et al., 2009), confirmed by

our results of soil residue analysis. Accordingly, literature values for the organic carbon normalized distribution coefficient (K_{OC}) and dissipation half-life values for atrazine show a wide range between 25 and 600 L kg^{-1} (Mudhoo, 2011) and a few days (PPDB, 2013) up to 433 days (Charnay et al., 2005). Latter authors found these highly varying half-life values even within a catchment of 135 ha, ranging from 22 to 433 days for surface soils.

Generally, variability in sorption and degradation behavior of atrazine can be attributed to different properties of the soils, experimental designs of laboratory studies and changing environmental conditions over time under natural field conditions. Various factors influence sorption of atrazine in the soils, such as pH, ionic strength, surface area, organic matter content, presence of microbial species, soil particle- and pore size and temperature, as reviewed by (Mudhoo, 2011). Degradation is mainly dependent on microbial activity (Charnay et al., 2005) and bioavailability, thus is closely linked to sorption, which is commonly considered as limiting factor for pesticide degradation. Referring to this, it was observed that atrazine aging, the increased pesticide-soil contact time, effects sorption-desorption processes, with higher sorption coefficients (K_d) for increasing incubation time (Pignatello and Huang, 1991). In this regard, there is a general agreement that a prolonged pesticide sorption time accompanied by the decreasing availability for its microbial degradation, leaching and plant uptake, results in a higher persistence (Barriuso et al., 2004). Hence, determined parameter values for atrazine persistence in soils highly depend on the incubation and hence sorption time for laboratory batch studies.

In concordance to this, recent findings of approximately two decades aged atrazine residues in field soils suggest that highest reported laboratory derived half-life values would underestimate found atrazine residue concentrations by far (Jablonowski et al., 2009) (results of this study, presented in chapter 4.2.4). Accordingly, atrazine and chemicals similar in nature might persist unexpectedly long in the environment. Consequently, the validity of sorption and degradation parameters obtained by batch experiments using standardized procedures (OECD, 2000) might be limited for risk assessments, what was stated by e.g. Vereecken et al. (2000). Latter authors also pointed to the fact that conditions for these batch

studies differ significantly from real-world conditions in field soils, in particular that under natural water flow conditions and pesticide transport in field soils the assumption of equilibrium sorption conditions for batch studies is unlikely to be valid. In consequence, non-equilibrium for pesticide sorption processes in soils during leaching may result in the underestimation of leached mass and hence the risk of groundwater contamination.

Summarizing, atrazine sorption in field soils on the long-term may be dynamic due to the various and changing environmental conditions, generally resulting in smaller dissipation parameter values for increasing atrazine-soil contact times. Atrazine dissipation in field soils rather follows biphasic (second or higher order kinetics) or multi-rate kinetics, dependent on sorption and hence bioavailability. In consequence, the accuracy of model predictions of catchment scale atrazine behavior on the long-term based on first-order-kinetics and static laboratory-derived sorption parameter values may be not reliable, even if the spatial variability of first-order dissipation parameter values and sorption K_d values have been exhaustively determined.

5.4 Final remarks

Atrazine groundwater monitoring and analysis of soil residue concentration two decades after its ban provides new insights on its environmental behavior on the long-term. Continuing atrazine groundwater concentration close to the threshold limit and soil residue concentration suggesting a significantly higher atrazine half-life value than found in literature challenge the validity of pesticide registration procedures. Mechanistic model approaches based on laboratory-derived pesticide sorption and degradation parameter values seem to be insufficient for predicting pesticide fate in the environment on the field scale and on the long-term. Thus the risk of atrazine adverse environmental effects remains hardly predictable and may be higher than estimated. In this respect it is important to mention that although atrazine is one of the most intensively studied pesticides there is a high uncertainty about its environmental fate. Considering the quantity of more than 1100 pesticides in use worldwide

and a lag of knowledge about their individual environmental fate suggested by the findings of this study, toxic effects on ecosystems on the long-term caused by the sum of all locally applied pesticides are difficult to determine and remain – to this day – unpredictable. Concluding, pesticide registration needs besides standard model predictions new approaches for evaluating the safe use of pesticides and strategies to reduce or avoid its use successively.

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Appendix A: Groundwater monitoring

Table 13: Laboratory data of groundwater analysis. Column title nomenclature: See "Abbreviations and Symbols" (page 17)

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20218	24.10.1991	< 0.01	< 0.02	< 0.02	< 0.01						
20235	24.10.1991	< 0.01	< 0.02	< 0.02	< 0.01						
20233	30.10.1991	< 0.01			< 0.01						
20224	30.10.1991	< 0.01	< 0.02	< 0.02	< 0.01						
20225	30.10.1991	< 0.01	< 0.02	< 0.02	< 0.01						
20228	30.10.1991	< 0.01	< 0.02	< 0.02	< 0.01						
20231	30.10.1991	< 0.01	< 0.02	< 0.02	< 0.01						
20230	07.11.1991	< 0.01	< 0.02	< 0.02	< 0.01						
20232	07.11.1991	0.06	< 0.02	< 0.02	0.04						
20234	07.11.1991	< 0.01	< 0.02	< 0.02	< 0.01						
20250	07.11.1991	< 0.01	< 0.02	< 0.02	< 0.01						
20251	07.11.1991	< 0.01	< 0.02	< 0.02	< 0.01						
20220	23.01.1992	0.07	0.02	< 0.02	0.01	< 0.02					
20221	23.01.1992	< 0.01	< 0.02	< 0.02	< 0.01	< 0.02					
20266	31.03.1992	0.02	< 0.02	< 0.02	0.01						
20267	31.03.1992	0.09	0.03	< 0.02	0.07						
960191	06.01.1993	< 0.05	< 0.05		< 0.05	< 0.05					
927931	12.01.1993	0.06	0.12		< 0.05	< 0.05					
40853	12.04.1994	< 0.05			< 0.05	< 0.05					
40712	12.04.1994	< 0.05			< 0.05	< 0.05					
960201	15.07.1994	< 0.05	< 0.05		< 0.05	< 0.05					
927931	18.07.1994	0.11	0.11		< 0.05	0.1					
927931	09.01.1995	0.08	< 0.05		< 0.05	0.06					
927761	10.01.1995	0.1	0.06		0.1	< 0.05					
960191	10.01.1995	< 0.05	< 0.05		< 0.05	< 0.05					
960201	27.06.1995	< 0.05	< 0.05	0.1	< 0.05	< 0.05					
40853	25.04.1997	0.056			< 0.05	< 0.05					
40712	25.04.1997	0.069			0.151	< 0.05					
40853	12.03.1998	0.08			0.035	< 0.05					
40712	12.03.1998	0.1			0.194	< 0.05					
20232	12.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20233	12.01.2000	0.2	0.06	0.07	0.43						
20197	13.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20242	13.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20250	13.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						
1691	14.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20218	14.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20244	14.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20254	14.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20267	14.01.2000	0.08	< 0.05	< 0.05	0.12						
20204	17.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20220	17.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20221	17.01.2000	< 0.05	< 0.05	< 0.05	< 0.05						
40712	10.05.2000	0.13									
20111	10.05.2000	0.08	0.06	< 0.05							
20232	10.05.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20233	10.05.2000	0.17	0.05	0.11	0.36						
20250	10.05.2000	< 0.05	< 0.05	< 0.05	< 0.05						
1691	11.05.2000	0.07	0.07	< 0.05	< 0.05						
20204	11.05.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20242	11.05.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20267	11.05.2000	0.06	< 0.05	< 0.05	0.11						
20211	12.05.2000	0.24	0.12	0.08							
20244	12.05.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20254	12.05.2000	0.05	< 0.05	< 0.05	< 0.05						
20220	15.05.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20205	16.05.2000	0.2	0.1	0.09							
20218	16.05.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20249	17.05.2000	0.11	0.05	< 0.05							
20197	18.05.2000	< 0.05	< 0.05	< 0.05	< 0.05						
20221	18.05.2000	< 0.05	< 0.05	< 0.05	< 0.05						
40853	09.11.2000	0.092			0.042	< 0.05					
40712	09.11.2000	0.15			0.155	< 0.05					
1691	17.01.2001	0.08	0.1	< 0.05	< 0.05						
20254	17.01.2001	< 0.05	< 0.05	< 0.05	< 0.05						
20249	19.01.2001	< 0.05	< 0.05	< 0.05	< 0.05						
20111	22.01.2001	< 0.05	0.06	< 0.05	< 0.05						
20267	22.01.2001	0.08	0.05	< 0.05	0.12						
20242	24.01.2001										
20220	01.02.2001										
20233	01.02.2001	0.16	0.08	0.07	0.39						
20204	08.02.2001										
20205	08.02.2001	< 0.05	< 0.05	< 0.05	< 0.05						
20211	08.02.2001	< 0.05	< 0.05	< 0.05	< 0.05						
20244	08.02.2001										
20232	09.02.2001										
20250	12.02.2001										
40853	03.04.2001	0.1			< 0.05	< 0.05					
40712	03.04.2001	0.145			0.157	< 0.05					
20242	19.09.2001	< 0.05	< 0.05	< 0.05	< 0.05						

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
-		µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
1352	04.12.2001	0.06	0.09	< 0.05	< 0.05						
20211	04.12.2001	< 0.05	< 0.05	< 0.05	< 0.05						
20232	04.12.2001	< 0.05	< 0.05	< 0.05	< 0.05						
20233	04.12.2001	0.18	0.11	0.14	0.34						
20243	04.12.2001	< 0.05	< 0.05	< 0.05	< 0.05						
20244	04.12.2001	< 0.05	< 0.05	< 0.05	< 0.05						
20203	30.01.2002	< 0.05	< 0.05	< 0.05	< 0.05						
20249	30.01.2002	< 0.05	< 0.05	< 0.05	< 0.05						
20254	30.01.2002	< 0.05	< 0.05	< 0.05	< 0.05						
20255	30.01.2002	< 0.05	< 0.05	< 0.05	< 0.05						
1691	04.03.2002	0.07	0.1	< 0.05	< 0.05						
20250	11.03.2002	< 0.05	< 0.05	< 0.05	< 0.05						
20111	18.03.2002	< 0.05	< 0.05	< 0.05	< 0.05						
20220	18.03.2002	< 0.05	< 0.05	< 0.05	< 0.05						
20197	26.03.2002	< 0.05	< 0.05	0.07	< 0.05						
20204	26.03.2002	< 0.05	< 0.05	< 0.05	< 0.05						
40853	27.03.2002	0.07			< 0.05	< 0.05					
40712	27.03.2002	0.13			0.14	< 0.05					
20205	27.03.2002	< 0.05	< 0.05	< 0.05	< 0.05						
20218	27.03.2002	< 0.05	< 0.05	< 0.05	< 0.05						
20267	27.03.2002	0.07	< 0.05	< 0.05	0.1						
20206	28.03.2002	< 0.05	0.11	< 0.05	< 0.05						
20251	08.04.2002	< 0.05	< 0.05	< 0.05	< 0.05						
20266	08.04.2002	< 0.05	< 0.05	< 0.05	< 0.05						
20231	09.04.2002	0.05	0.05	< 0.05	0.15						
20226	10.04.2002	0.05	< 0.05	< 0.05	0.09						
20230	10.04.2002	0.05	0.07	< 0.05	0.12						
873011	24.06.2002	0.06	0.05	< 0.05	< 0.05						
822901	19.07.2002	0.09	0.08	< 0.05	< 0.05						
870891	22.07.2002	< 0.05	< 0.05	< 0.05	< 0.05						
967151	22.07.2002	< 0.05	< 0.05	< 0.05	< 0.05						
927851	25.07.2002	< 0.05	< 0.05	< 0.05	< 0.05						
40712	02.04.2003	0.12									
1352	10.07.2003	0.07	0.07	< 0.05	< 0.05						
1691	10.07.2003	0.08	0.08	< 0.05	< 0.05						
873011	10.07.2003	0.08	0.07	< 0.05	< 0.05						
20230	14.07.2003	0.09	0.08	< 0.05	< 0.05						
20231	14.07.2003	0.08	0.07	< 0.05	< 0.05						
20232	14.07.2003	0.05	0.05	< 0.05	0.05						
20250	14.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20251	14.07.2003	0.08	0.05	< 0.05	< 0.05						
20266	14.07.2003	0.09	0.07	< 0.05	< 0.05						

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20203	15.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20211	15.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20242	15.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20244	15.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20249	15.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20254	15.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20111	18.07.2003	< 0.05	0.05	< 0.05	< 0.05						
20218	18.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20267	18.07.2003	0.09	< 0.05	< 0.05	0.1						
20197	21.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20204	21.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20205	21.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20220	21.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
822901	22.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
873051	22.07.2003	0.08	0.06	< 0.05	< 0.05						
20233	23.07.2003	0.09	0.05	< 0.05	0.24						
927851	23.07.2003	0.09	0.07	< 0.05	< 0.05						
967151	23.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20226	24.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20255	24.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
20206	29.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
870891	29.07.2003	< 0.05	< 0.05	< 0.05	< 0.05						
40712	28.04.2004	0.14									
927851	22.03.2005										
927851	22.03.2005						0.00		497	6.6	
927761	29.03.2005						66.80		919	6.8	
960361	29.03.2005						29.60		676	6.7	
822901	29.03.2005						48.70		924	6.7	
927931	31.03.2005						44.10		956	6.8	
40712	21.04.2005	0.112									
927851	12.07.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		459	7.3	
927761	12.07.2005	< 0.01	0.01	0.05	< 0.027	< 0.046	68.20		879	6.8	
927931	12.07.2005	0.09	0.1	< 0.01	< 0.027	0.02	45.60		985	7.0	
960361	12.07.2005	0.06	0.06	< 0.01	0.04	< 0.046	27.40		715	6.8	
822901	12.07.2005	0.11	0.09	< 0.01	< 0.027	0.03	46.90		950	6.9	
1691	12.07.2005	0.14	0.13	< 0.01	< 0.027	0.04	71.70		691	8.1	208
20111	12.07.2005	0.04	0.04	< 0.01	< 0.027	0.02	57.70	0.07	755		216
20266	12.07.2005	0.03	0.02	0.04	< 0.027	0.01	65.20	22.73	732		232
868921	12.07.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	12.07.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			810	6.4	
20219	13.07.2005	< 0.01	< 0.01	< 0.01	0.03	< 0.046	23.70	2.02	522		211
20220	13.07.2005	0.03	0.03	0.04	< 0.027	< 0.046	18.30		343		226

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20230	14.07.2005	0.15	0.09	0.17	0.16	0.05	66.50	1.01	687		229
20233	14.07.2005	0.12	0.06	0.08	0.19	0.04			760		
20251	15.07.2005	0.03	0.03	0.04	< 0.027	0.02			662		
20267	15.07.2005	0.03	0.02	< 0.01	0.04	< 0.046			620		
873011	21.07.2005	0.03	0.03	< 0.01	< 0.027	< 0.046			709		
873051	21.07.2005	0.12	0.11	< 0.01	< 0.027	0.02			727		
100390	21.07.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
927851	23.08.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		415	6.8	
927761	23.08.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	67.30		922	6.8	
927931	23.08.2005	0.08	0.11	< 0.01	< 0.027	< 0.046	45.20		746	6.9	
960361	23.08.2005	< 0.01	< 0.01	< 0.01	0.11	< 0.046	36.10		741	6.6	
822901	23.08.2005	0.08	0.1	< 0.01	< 0.027	< 0.046	46.50		932	6.9	
868921	23.08.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	23.08.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			701	6.2	
1691	26.08.2005	0.09	0.11	< 0.01	< 0.027	< 0.046			713		
20219	26.08.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			530		
20220	26.08.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			331		
20230	29.08.2005	0.1	0.06	0.16	0.19	< 0.046			665		
20267	29.08.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			617		
20111	30.08.2005	< 0.01	0.04	< 0.01	< 0.027	< 0.046			751		
20233	30.08.2005	0.09	0.07	0.07	0.25	< 0.046			758		
20266	30.08.2005	< 0.01	0.01	0.04	< 0.027	< 0.046			733		
100392	31.08.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
100390	31.08.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
873011	07.09.2005	0.03	0.06	< 0.01	< 0.027	< 0.046			716		
873051	07.09.2005	0.16	0.13	< 0.01	< 0.027	< 0.046			731		
20251	08.09.2005	< 0.01	0.02	< 0.01	< 0.027	< 0.046			652		
927851	15.09.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		796	7.2	
927761	15.09.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	66.80		922	6.8	
927931	15.09.2005	0.08	0.11	< 0.01	< 0.027	< 0.046	45.20		985	7.0	
960361	15.09.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	37.60		765	6.7	
822901	15.09.2005	0.08	0.1	< 0.01	< 0.027	< 0.046	46.90		955	6.9	
868921	15.09.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	15.09.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			854	6.3	
20111	10.10.2005	0.04	0.05	< 0.01	< 0.027	0.03			762		
20230	10.10.2005	0.07	0.07	< 0.01	< 0.027	0.03			652		
20233	10.10.2005	0.13	0.07	0.09	0.2	0.04			704		
873011	10.10.2005	0.13	0.07	< 0.01	0.14	0.04			722		
873051	10.10.2005	0.18	0.15	< 0.01	< 0.027	0.04			752		
1691	11.10.2005	0.14	0.12	< 0.01	< 0.027	0.04			708		
20251	11.10.2005	0.03	0.03	0.02	< 0.027	0.02			644		
20267	11.10.2005	0.03	0.01	< 0.01	0.04	< 0.046			597		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
-		µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20219	12.10.2005	0.03	0.038	0.04	< 0.027	0.01			447		
20220	12.10.2005	0.02	0.01	0.04	< 0.027	< 0.046			360		
20266	12.10.2005	0.03	0.01	0.04	< 0.027	0.01			739		
100392	20.10.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
100390	20.10.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
927851	27.10.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		435	7.2	64
927761	27.10.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	64.20		818	6.8	194
927931	27.10.2005	0.05	0.1	< 0.01	< 0.027	< 0.046	44.30		955	6.9	100
960361	27.10.2005	0.08	< 0.01	< 0.01	< 0.027	< 0.046	43.20		780	6.5	165
822901	27.10.2005	0.09	0.1	< 0.01	< 0.027	< 0.046	46.50		927	6.8	130
868921	27.10.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	27.10.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			761	6.3	55
20233	03.11.2005	0.14	0.07	< 0.01	0.24	< 0.046	53.20	4.29	705	6.7	203
20266	03.11.2005	0.03	0.01	0.04	< 0.027	< 0.046	64.10	0.63	729	6.7	160
1691	09.11.2005	0.16	0.12	< 0.01	< 0.027	< 0.046	67.50	3.29	696	6.7	181
20219	09.11.2005	0.03	0.038	0.04	< 0.027	< 0.046	12.30	3.23	448	7.3	208
20220	09.11.2005	0.01	< 0.01	< 0.01	< 0.027	< 0.046	14.60		348	5.4	185
873051	09.11.2005	0.17	0.13	< 0.01	< 0.027	< 0.046	66.00		758	6.6	264
100392	09.11.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	24.30	1.19		6.8	235
100390	09.11.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	17.70	0.00		6.5	237
873011	10.11.2005	0.06	0.06	0.04	< 0.027	< 0.046	89.60	41.70	726	6.7	169
20111	14.11.2005	0.09	0.04	0.03	0.07	0.03	68.00	1.20	762	6.8	240
20230	14.11.2005	0.14	0.07	0.16	0.19	0.05	64.40		613	6.9	238
20251	14.11.2005	0.03	0.03	0.03	< 0.027	0.03	68.40		614	6.5	234
20267	14.11.2005	0.02	0.01	0.04	< 0.027	< 0.046	21.30		606	6.8	245
927851	16.11.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		480	7.1	-60
927761	16.11.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	65.50		915	6.9	90
927931	16.11.2005	0.1	0.1	< 0.01	< 0.027	< 0.046	44.70		451	7.1	73
960361	16.11.2005	0.07	< 0.01	< 0.01	< 0.027	< 0.046	43.40		786	6.8	101
822901	16.11.2005	0.1	0.1	< 0.01	< 0.027	< 0.046	46.90		921	7.0	107
868921	16.11.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	16.11.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			850	6.4	-30
20219	01.12.2005	0.04	0.038	0.04	< 0.027	0.01	27.10	2.34	399	7.1	269
20230	01.12.2005	0.13	0.06	< 0.01	0.17	0.04	50.50	1.39	615	6.7	266
873051	01.12.2005	0.21	0.17	< 0.01	< 0.027	0.05	58.60	1.93	698	6.0	272
1691	06.12.2005	0.14	0.12	< 0.01	< 0.027	0.04	59.40		671	6.7	262
20233	06.12.2005	0.12	0.08	< 0.01	0.2	0.05	52.40		714	6.7	268
20267	06.12.2005	0.02	0.01	< 0.01	0.03	< 0.046	19.90	1.37	598	6.0	280
873011	08.12.2005	0.06	0.06	0.04	< 0.027	0.03	74.30	0.00	696	6.6	270
20111	13.12.2005	0.04	0.04	< 0.01	< 0.027	0.02	50.50	1.95	722	6.7	152
20220	13.12.2005	0.02	0.01	< 0.01	< 0.027	< 0.046	13.50	1.42	340	6.2	121
20251	13.12.2005	0.02	0.02	0.05	< 0.027	0.01	30.80	1.59	610	6.3	239

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
-		µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20266	13.12.2005	0.03	0.02	0.04	< 0.027	0.01	57.10		685	6.7	235
927851	14.12.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		436	6.9	-61
927761	14.12.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	63.30		805	6.7	101
927931	14.12.2005	0.11	0.11	< 0.01	< 0.027	< 0.046	43.60		970	7.0	80
960361	14.12.2005	0.08	< 0.01	< 0.01	< 0.027	< 0.046	46.50		785	6.8	130
822901	14.12.2005	0.11	0.11	< 0.01	< 0.027	< 0.046	46.00		930	7.0	125
868921	14.12.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	14.12.2005	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			750	6.3	-27
20219	10.01.2006	0.04	0.038	0.04	< 0.027	0.02	31.70	2.85	364	6.9	209
20230	10.01.2006	0.13	0.07	0.12	0.15	0.05	62.30	3.19	601	6.6	252
20233	10.01.2006	0.14	0.07	0.08	0.21	0.05	63.40	4.68	660	6.9	253
873051	10.01.2006	0.17	0.13	< 0.01	< 0.027	< 0.046	92.10	6.32	660	6.6	243
20111	13.01.2006	0.05	0.05	< 0.01	< 0.027	0.03	56.60	4.83	720	6.8	224
20251	13.01.2006	0.03	0.03	0.02	< 0.027	0.03	72.50	3.29	611	6.5	248
20266	13.01.2006	< 0.01	< 0.01	0.12	< 0.027	< 0.046	34.40	2.90	682	6.6	310
927851	16.01.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		438	6.2	-58
927761	16.01.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	65.50		812	6.8	117
927931	16.01.2006	0.11	0.1	< 0.01	< 0.027	< 0.046	45.20		940	7.0	75
960361	16.01.2006	0.07	< 0.01	< 0.01	0.05	< 0.046	44.30		750	6.8	135
822901	16.01.2006	0.12	0.11	< 0.01	< 0.027	< 0.046	47.80		915	7.0	120
1691	16.01.2006	0.13	0.12	< 0.01	< 0.027	< 0.046	73.90	2.59	668	6.7	309
20220	16.01.2006	0.03	< 0.01	< 0.01	< 0.027	0.01	13.70	2.12	348	6.2	285
20267	16.01.2006	0.03	0.02	< 0.01	0.03	< 0.046	30.20	4.34	615	6.6	245
873011	16.01.2006	0.07	0.08	< 0.01	< 0.027	0.03	69.40	6.71	715	6.7	240
868921	16.01.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	16.01.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			751	6.3	-23
1691	14.02.2006	0.14	0.12	< 0.01	< 0.027	0.04	72.00	7.12	635	6.6	224
20220	14.02.2006	0.02	0.01	0.04	< 0.027	< 0.046			342		
20251	14.02.2006	0.03	0.04	0.04	< 0.027	0.02	72.70	6.39	575	6.4	228
20266	14.02.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	34.90	8.18	666	6.3	228
927851	15.02.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		451	7.0	-69
927761	15.02.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	64.60		844	6.9	99
927931	15.02.2006	0.09	0.09	< 0.01	< 0.027	< 0.046	44.70		950	7.0	70
960361	15.02.2006	0.06	< 0.01	< 0.01	< 0.027	< 0.046	36.80		700	6.8	150
822901	15.02.2006	0.12	0.11	< 0.01	< 0.027	< 0.046	46.90		920	7.0	110
868921	15.02.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	15.02.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			780	6.4	-23
20219	16.02.2006	0.04	0.02	0.02	0.03	0.02	31.50	4.24	390	6.9	218
20230	16.02.2006	0.14	0.07	0.07	0.16	0.05	62.50	2.40	606	6.7	221
20233	16.02.2006	0.14	0.07	< 0.01	0.21	0.05	69.90	4.24	660	6.7	224
873051	16.02.2006	0.18	0.14	< 0.01	< 0.027	0.04	70.00	12.59	653	6.6	235
20111	20.02.2006	< 0.01	0.06	< 0.01	< 0.027	0.04	58.80	3.88	698	6.8	242

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20267	20.02.2006	0.04	0.06	< 0.01	< 0.027	0.03	61.90	5.42	599	6.8	263
873011	20.02.2006	0.07	0.08	0.04	< 0.027	0.03	92.20	5.50	692	6.6	267
927851	15.03.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		459	7.0	-70
927761	15.03.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	63.30		843	6.9	94
927931	15.03.2006	0.11	0.09	< 0.01	< 0.027	< 0.046	44.00		955	7.0	70
960361	15.03.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	21.00		615	7.1	150
822901	15.03.2006	0.11	0.09	< 0.01	< 0.027	< 0.046	45.20		925	6.9	115
20219	15.03.2006	0.03	0.08	< 0.01	0.03	0.02	18.40		371	6.9	185
20230	15.03.2006	0.14	0.07	< 0.01	0.31	0.04	60.70	0.00	613	6.7	176
868921	15.03.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	15.03.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			794	6.4	-27
1691	16.03.2006	0.15	0.12	< 0.01	< 0.027	0.04	67.90	14.08	589	6.8	172
20233	16.03.2006	0.13	0.07	< 0.01	0.43	0.05	22.50	1.75	626	6.6	187
873051	16.03.2006	0.17	0.13	< 0.01	< 0.027	0.04	69.10	2.74	626	6.7	215
20220	17.03.2006	0.02	0.01	< 0.01	0.03	< 0.046	13.80	2.29	339	6.1	211
20251	17.03.2006	0.04	0.03	< 0.01	0.03	0.03	72.40	0.63	536	6.4	206
20266	17.03.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	35.10	1.88	638	6.3	219
20111	20.03.2006	0.04	0.05	< 0.01	< 0.027	0.03	58.70	2.75	687	6.7	200
20267	20.03.2006	0.04	0.05	< 0.01	< 0.027	0.03	50.80	1.49	580	6.7	193
873011	20.03.2006	0.08	0.06	< 0.01	0.03	0.03	61.70	1.96	680	6.6	207
40712	11.04.2006	0.26									
927931	11.04.2006	0.11	0.09	< 0.01	< 0.027	< 0.046	45.60		940	7.0	65
960361	11.04.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	23.30		640	7.1	130
822901	11.04.2006	0.1	0.08	< 0.01	< 0.027	< 0.046	45.60		910	7.0	100
927851	12.04.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		475	7.0	-50
927761	12.04.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	63.70		900	6.9	75
868921	12.04.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	12.04.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			845	6.4	-10
20230	21.04.2006	0.13	0.07	0.12	0.16	0.04	61.90	1.19	639	6.6	234
20233	21.04.2006	0.13	0.07	0.04	0.2	0.05	71.60		710	6.7	239
873011	21.04.2006	0.06	0.06	0.04	< 0.027	0.02	91.90	65.19	733	6.7	262
1691	24.04.2006	0.14	0.12	< 0.01	< 0.027	0.04	69.00	6.53	631	6.7	276
20111	24.04.2006	0.02	0.05	< 0.01	< 0.027	0.03	59.50	43.76	736	6.7	275
20267	24.04.2006	0.05	0.038	0.04	< 0.027	0.03	58.70		618	6.8	264
873051	24.04.2006	0.17	0.13	< 0.01	< 0.027	0.04	69.80	13.44	650	6.2	273
20219	25.04.2006	0.02	0.038	0.04	< 0.027	< 0.046	28.60		395	7.0	227
20220	25.04.2006	0.02	0.01	0.04	< 0.027	< 0.046	14.40	0.86	329	6.1	206
20251	26.04.2006	0.03	0.03	0.04	< 0.027	0.02	71.70	9.08	612	6.4	219
20266	26.04.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	33.80	0.69	668	6.3	228
927851	15.05.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		457	7.2	-46
927761	15.05.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	64.60		830	7.1	88
927931	15.05.2006	0.11	0.1	< 0.01	< 0.027	< 0.046	45.60		950	7.1	75

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
960361	15.05.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	27.20		660	7.1	100
822901	15.05.2006	0.12	0.09	< 0.01	< 0.027	< 0.046	46.50		915	7.0	95
868921	15.05.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	15.05.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			792	6.5	-26
20230	18.05.2006	0.13	0.07	0.16	0.16	0.04	62.80	2.24	632	7.6	210
20233	18.05.2006	0.12	0.07	0.1	0.2	0.04	69.10	2.91	708	6.7	240
873051	18.05.2006	0.17	0.13	< 0.01	< 0.027	0.04	69.60	7.12	642	6.7	230
100392	18.05.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	41.80	5.74		6.6	243
100390	18.05.2006	< 0.01	0.038	0.04	< 0.027	< 0.046	45.10	2.91		6.7	240
20111	21.05.2006	0.04	0.04	< 0.01	< 0.027	0.03	59.10		732	6.8	240
873011	21.05.2006	0.06	0.06	0.04	< 0.027	0.02	89.40	0.00	686	6.6	250
20251	22.05.2006	0.03	0.03	0.04	< 0.027	0.02	64.80		625	6.5	250
20266	22.05.2006	< 0.01	< 0.01	0.06	< 0.027	< 0.046	37.80		666	6.3	245
20267	22.05.2006	0.04	0.06	< 0.01	< 0.027	0.03	55.30		612	6.8	232
1691	23.05.2006	0.13	0.11	< 0.01	< 0.027	0.04	65.20		645	6.7	248
20219	23.05.2006	0.02	0.02	0.04	< 0.027	0.01	20.70	2.05	378	6.2	265
20220	23.05.2006	0.02	0.02	0.04	< 0.027	< 0.046	21.70	0.16	321	6.0	256
927851	13.06.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		487	7.1	-61
927761	13.06.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	63.30		895	6.8	91
927931	13.06.2006	0.11	0.1	< 0.01	< 0.027	< 0.046	44.70		935	7.1	75
960361	13.06.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	24.30		680	7.0	100
822901	13.06.2006	0.13	0.1	< 0.01	< 0.027	< 0.046	45.60		900	7.0	110
868921	13.06.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	13.06.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			840	6.3	-23
100392	19.06.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046		1.92		6.5	236
100390	19.06.2006	< 0.01	0.02	0.07	< 0.027	< 0.046		2.12		6.5	222
1691	20.06.2006	0.12	0.11	< 0.01	< 0.027	0.03	64.50		685	6.6	191
20219	20.06.2006	0.02	0.01	< 0.01	< 0.027	< 0.046	14.00	1.94	378	6.1	138
20220	20.06.2006	0.02	0.01	< 0.01	< 0.027	< 0.046	20.10	2.10	323	6.1	149
20233	20.06.2006	0.13	0.07	0.13	0.22	0.04	64.10	1.78	698	6.6	153
873011	20.06.2006	0.06	0.07	< 0.01	< 0.027	0.02	87.40	0.00	696	6.6	162
20111	21.06.2006	0.03	0.03	< 0.01	< 0.027	0.02	53.70		729	6.8	158
20230	21.06.2006	0.07	0.04	0.11	0.11	0.02	51.80	0.50	609	6.7	142
20251	21.06.2006	0.02	0.03	0.02	< 0.027	0.02	65.70		621	6.5	153
20266	21.06.2006	< 0.01	< 0.01	0.13	< 0.027	< 0.046	32.80	1.46	670	6.3	160
20267	21.06.2006	0.04	0.05	< 0.01	< 0.027	0.02	52.30		618	6.8	155
873051	21.06.2006	0.15	0.12	< 0.01	< 0.027	0.03	64.40	1.14	699	6.7	157
927931	17.07.2006	0.09	0.1	< 0.01	< 0.027	< 0.046	44.70		930	7.1	80
960361	17.07.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	28.20		685	6.9	70
822901	17.07.2006	0.1	0.09	< 0.01	< 0.027	< 0.046	45.20		905	7.1	105
927851	18.07.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		465	7.2	-60
927761	18.07.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	63.70		890	7.0	115

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
868921	18.07.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	18.07.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			825	6.5	-25
20219	20.07.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	17.20	1.11	371	6.0	181
20220	20.07.2006	0.02	< 0.01	< 0.01	< 0.027	< 0.046	12.80	1.41	326	5.9	190
20251	20.07.2006	0.02	0.04	0.04	< 0.027	0.02	66.40	1.06	630	6.4	178
20266	20.07.2006	< 0.01	< 0.01	0.1	< 0.027	< 0.046	34.40	2.25	670	6.2	182
100392	20.07.2006	0.2	0.15	< 0.01	< 0.027	0.05	15.70	1.50		6.3	184
100390	20.07.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	14.50	2.16		6.4	184
20111	21.07.2006	0.04	0.04	< 0.01	< 0.027	0.02	60.00	1.54	742	6.7	173
20230	21.07.2006	0.03	0.03	0.04	< 0.027	0.02	82.90	1.87	615	6.5	177
20267	21.07.2006	0.04	0.05	< 0.01	< 0.027	0.02	57.20	1.70	621	6.7	172
1691	24.07.2006	0.15	0.11	< 0.01	< 0.027	0.03	59.00	1.29	678	6.6	172
20233	25.07.2006	0.13	0.09	0.12	0.21	0.04	65.70		696	6.6	172
873011	25.07.2006	0.13	0.11	0.04	< 0.027	< 0.046	95.10	2.40	694	6.5	174
873051	26.07.2006	0.2	0.15	< 0.01	< 0.027	0.05	64.50	2.10	695	6.6	176
927851	16.08.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00		424	7.1	-46
927761	16.08.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	65.10		760	6.8	102
927931	16.08.2006	0.09	0.09	< 0.01	< 0.027	< 0.046	46.90		940	7.1	90
960361	16.08.2006	< 0.01	< 0.01	< 0.01	0.05	< 0.046	37.00		735	6.8	80
822901	16.08.2006	0.11	0.1	< 0.01	< 0.027	< 0.046	47.80		915	7.0	115
868921	16.08.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
868921	16.08.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046			721	6.3	-30
100390	21.08.2006	< 0.01	0.038	0.04	< 0.027	< 0.046	37.20	0.91		6.5	215
100392	21.08.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	27.80	0.99		6.5	215
20233	22.08.2006	0.15	0.07	0.17	0.23	0.05	72.20	0.97	696	6.8	160
20251	22.08.2006	0.03	0.03	0.03	< 0.027	0.03	75.10	0.42	629	6.5	199
20266	22.08.2006	< 0.01	< 0.01	0.19	< 0.027	< 0.046	36.30	1.64	669	6.5	206
873011	22.08.2006	0.06	0.06	< 0.01	< 0.027	0.03	97.10	2.42	694	6.7	191
873051	22.08.2006	0.2	0.15	< 0.01	< 0.027	0.05	71.20	2.21	696	6.9	184
20111	23.08.2006	0.04	0.04	< 0.01	< 0.027	0.03	65.90	0.28	738	6.9	172
20219	23.08.2006	0.02	0.038	0.04	< 0.027	< 0.046	6.50	0.99	373	6.3	189
20220	23.08.2006	0.02	0.01	0.04	< 0.027	< 0.046	24.30	0.95	326	6.2	191
20230	23.08.2006	0.13	0.06	0.19	0.18	0.04	56.70	0.92	596	6.8	170
20267	23.08.2006	0.04	0.05	< 0.01	< 0.027	0.03	58.60	1.77	621	6.9	155
1691	24.08.2006	0.15	0.13	< 0.01	< 0.027	0.04	69.30	1.56	680	7.0	149
20233	14.09.2006	0.11	0.07	0.08	0.16	0.03	65.60	9.35	699	6.8	239
868921	14.09.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
20230	15.09.2006	0.11	0.05	0.14	0.15	0.03	52.80	5.14	615	6.8	227
873051	15.09.2006	0.18	0.16	< 0.01	< 0.027	0.04	64.80	6.56	736	6.8	237
20111	18.09.2006	0.04	0.06	< 0.01	< 0.027	0.03	57.60	10.15	735	6.8	235
20219	18.09.2006	0.02	0.03	0.04	< 0.027	< 0.046	20.90	1.52	375	6.3	168
20220	18.09.2006	0.02	0.03	0.02	< 0.027	< 0.046	21.80	1.57	326	6.2	145

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
-		µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20251	18.09.2006	0.03	0.05	0.04	< 0.027	0.03	67.90	5.91	638	6.5	196
20266	18.09.2006	< 0.01	0.02	0.15	< 0.027	< 0.046	37.70	2.99	671	6.4	230
20267	18.09.2006	0.04	0.06	< 0.01	< 0.027	0.02	54.30	7.04	624	6.8	226
100390	20.09.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	19.10	4.67		6.6	229
1691	20.09.2006	0.14	0.11	< 0.01	< 0.027	0.03	64.90	6.92	709	6.8	225
873011	20.09.2006	0.05	0.06	< 0.01	< 0.027	0.02	87.00	5.85	730	6.6	226
100392	20.09.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	16.60	3.86		6.6	230
100390	16.10.2006	0.01	< 0.01	< 0.01	< 0.027	< 0.046	14.90	0.00		6.7	214
1691	16.10.2006	0.15	0.11	< 0.01	< 0.027	0.04	65.10		704	6.9	217
100392	16.10.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	14.00	0.00		6.7	218
20233	17.10.2006	0.12	0.07	0.1	0.22	0.04	66.00	1.54	680	6.8	201
873011	17.10.2006	0.06	0.06	< 0.01	< 0.027	0.02	86.80	1.33	735	6.8	200
20219	23.10.2006	0.02	0.02	< 0.01	< 0.027	< 0.046	5.58	1.64	378	6.4	70
20220	23.10.2006	0.02	0.02	< 0.01	< 0.027	< 0.046	21.60	0.00	337	6.3	124
20251	23.10.2006	0.03	0.03	0.02	< 0.027	0.02	65.40	0.08	640	6.5	226
822921	24.10.2006	0.03	0.01	0.04	< 0.027	< 0.046	85.90				
841201	24.10.2006	< 0.01	0.02	< 0.01	< 0.027	0.01	57.50				
820551	24.10.2006	0.38	0.35	0.14	0.08	0.06	60.20				
20111	24.10.2006	0.04	0.05	< 0.01	< 0.027	0.03	57.70	1.34	726	7.0	131
20230	24.10.2006	0.11	0.05	0.12	0.17	0.03	53.20	0.01	608	7.1	148
20266	24.10.2006	0.04	0.05	< 0.01	< 0.027	0.03	38.60	1.35	678	6.4	148
20267	24.10.2006	0.04	0.04	< 0.01	< 0.027	0.02	57.40	3.79	625	7.0	142
873051	24.10.2006	0.23	0.16	< 0.01	< 0.027	0.05	65.40	2.29	737	7.1	144
868921	24.10.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
40782	25.10.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	59.80				
40787	25.10.2006	0.01	0.04	< 0.01	< 0.027	< 0.046	46.90				
40789	25.10.2006	< 0.01	0.03	< 0.01	< 0.027	< 0.046	53.60				
873441	26.10.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	22.00				
967271	26.10.2006	0.21	0.14	0.03	< 0.027	0.03	92.50				
40780	26.10.2006	0.01	0.02	< 0.01	< 0.027	< 0.046	46.50				
868921	13.11.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
40780	14.11.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	46.90				
40782	14.11.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	59.80				
40787	14.11.2006	< 0.01	0.02	< 0.01	< 0.027	< 0.046	54.00				
873441	15.11.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	20.80				
967271	15.11.2006	0.06	0.04	< 0.01	< 0.027	< 0.046	96.10				
841201	15.11.2006	< 0.01	0.01	< 0.01	< 0.027	< 0.046	46.00				
40789	15.11.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	53.60				
820551	15.11.2006	0.19	0.18	0.06	0.04	0.02	60.20				
100390	20.11.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	17.80	6.25		6.8	255
822921	20.11.2006	0.02	0.01	0.04	< 0.027	< 0.046	85.00				
20111	20.11.2006	0.02	0.03	< 0.01	< 0.027	< 0.046	60.30	11.02	732	7.1	207

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
-		µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20233	20.11.2006	0.09	0.05	0.03	0.15	0.02	48.30	9.09	682	6.9	199
20267	20.11.2006	0.03	< 0.01	< 0.01	< 0.027	0.01	59.70	9.30	632	7.0	196
100392	20.11.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	16.20	6.25		6.8	226
20230	22.11.2006	0.09	0.04	< 0.01	0.13	0.02	54.50	2.51	573	7.0	194
873011	22.11.2006	0.04	0.05	< 0.01	< 0.027	< 0.046	88.90	0.00	717	6.8	199
873051	22.11.2006	0.22	0.15	< 0.01	< 0.027	0.04	67.80	5.79	734	7.0	194
1691	23.11.2006	0.14	0.11	< 0.01	< 0.027	0.03	67.80	8.20	685	6.9	193
20251	23.11.2006	0.02	0.02	0.04	< 0.027	0.02	70.10	2.91	634	6.7	196
20266	23.11.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	42.70	4.43	674	6.5	199
100390	06.12.2006	0.01	0.038	0.04	< 0.027	< 0.046		5.96		6.8	243
100392	06.12.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046		6.82		6.8	241
20111	12.12.2006	0.03	0.03	0.04	< 0.027	0.02	69.50	3.30	739	6.7	210
20251	12.12.2006	0.02	0.03	0.03	< 0.027	0.02	70.10	6.60	638	6.7	234
20266	12.12.2006	< 0.01	< 0.01	0.12	< 0.027	< 0.046	40.50	7.19	676	6.5	211
20267	12.12.2006	< 0.01	< 0.01	0.1	< 0.027	< 0.046	40.50	0.00	637	6.5	215
873011	12.12.2006	0.06	0.06	0.04	< 0.027	0.02	86.90	0.00	723	6.9	213
873441	14.12.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	16.60				
841201	14.12.2006	< 0.01	0.02	< 0.01	< 0.027	0.01	53.60				
40787	14.12.2006	0.01	0.02	< 0.01	< 0.027	< 0.046	42.10				
40789	14.12.2006	< 0.01	0.01	< 0.01	< 0.027	< 0.046	49.60				
20230	14.12.2006	0.1	0.05	0.13	0.13	0.03	53.20	2.54	608	7.1	223
20233	14.12.2006	0.11	0.06	0.1	0.18	0.04	65.70	8.95	671	6.9	190
873051	14.12.2006	0.2	0.14	< 0.01	< 0.027	0.04	66.00	9.32	736	6.9	203
40780	15.12.2006	0.01	0.02	< 0.01	< 0.027	< 0.046	51.40				
820551	15.12.2006	0.35	0.31	0.12	0.07	0.05	66.00				
1691	15.12.2006	0.13	0.11	< 0.01	< 0.027	0.03	66.00	11.03	685	7.0	222
868921	15.12.2006	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
822921	18.12.2006	< 0.01	0.02	< 0.01	< 0.027	< 0.046	94.70				
967271	18.12.2006	< 0.01	0.13	< 0.01	< 0.027	< 0.046	110.20				
40782	18.12.2006	< 0.01	0.02	< 0.01	< 0.027	< 0.046	66.00				
20111	15.01.2007	0.03	0.02	< 0.01	< 0.027	0.02	57.90	3.58	717	7.0	256
20251	15.01.2007	0.03	0.03	0.04	< 0.027	0.01	69.50	2.53	579	6.6	291
20266	15.01.2007	< 0.01	< 0.01	0.03	< 0.027	< 0.046	36.00	3.21	666	6.3	308
20267	15.01.2007	0.04	0.04	< 0.01	< 0.027	0.02	57.60	5.89	621	7.0	250
873011	15.01.2007	0.05	0.05	< 0.01	< 0.027	0.02	66.80	5.72	706	6.8	275
822921	17.01.2007	0.02	0.01	0.04	< 0.027	< 0.046	85.90				
873441	18.01.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	20.90				
820551	18.01.2007	0.37	0.34	0.12	0.08	0.05	59.80				
868921	18.01.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
1691	19.01.2007	0.13	0.1	< 0.01	< 0.027	< 0.046	61.80	6.39	601	7.0	240
967271	22.01.2007	0.17	0.09	0.04	< 0.027	0.02	103.60				
841201	22.01.2007	< 0.01	0.02	< 0.01	< 0.027	< 0.046	58.00				

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
40782	22.01.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	60.60				
40787	22.01.2007	0.01	0.02	0.05	< 0.027	< 0.046	47.40				
40780	23.01.2007	0.01	0.01	< 0.01	< 0.027	< 0.046	46.90				
20219	25.01.2007	0.01	0.038	0.04	< 0.027	< 0.046	20.80	3.20	376	6.6	244
20220	25.01.2007	0.02	0.038	0.04	< 0.027	< 0.046	22.30	1.89	324	6.6	240
20230	30.01.2007	0.1	0.05	0.13	0.14	0.03	53.00	4.30	582	6.8	217
20233	30.01.2007	0.11	0.05	0.08	0.18	0.03	65.20	10.42	670	6.8	219
873051	30.01.2007	0.19	0.12	< 0.01	< 0.027	0.03	66.80	0.45	679	6.8	227
40782	13.02.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	60.20				
40787	13.02.2007	< 0.01	0.01	0.05	< 0.027	< 0.046	46.00				
40789	13.02.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	54.00				
820551	13.02.2007	0.5	0.39	0.16	0.1	0.06	61.50				
868921	13.02.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
873441	14.02.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	35.50				
822921	14.02.2007	0.03	0.02	0.04	< 0.027	< 0.046	86.80				
967271	14.02.2007	0.15	0.08	0.04	< 0.027	0.02	116.90				
841201	14.02.2007	< 0.01	0.02	< 0.01	< 0.027	0.01	58.00				
40780	16.02.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	46.50				
20219	21.02.2007	0.02	0.038	0.04	< 0.027	< 0.046	11.40	2.80	377	6.2	291
20220	21.02.2007	0.02	0.038	0.04	< 0.027	< 0.046	26.90	4.11	332	6.0	176
20251	21.02.2007	0.02	0.03	0.04	< 0.027	0.02	63.60	7.63	633	6.4	303
20266	21.02.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	40.80	4.99	666	6.3	319
873011	21.02.2007	0.07	0.06	0.04	< 0.027	0.02	85.70	6.79	721	6.8	288
1691	22.02.2007	0.15	0.12	< 0.01	< 0.027	0.04	64.30	8.47	689	7.0	183
20230	22.02.2007	0.1	0.05	< 0.01	0.14	0.03	52.70	5.83	580	6.7	181
20233	22.02.2007	0.12	0.06	< 0.01	0.19	0.04	65.70	5.83	674	6.7	181
873051	22.02.2007	0.17	0.13	0.04	< 0.027	0.03	66.70	4.53	673	6.7	186
20111	23.02.2007	0.02	0.04	< 0.01	< 0.027	0.02	58.40	9.29	710	6.8	186
20267	23.02.2007	0.04	0.05	0.04	< 0.027	0.02	55.50	8.23	617	6.2	179
868921	14.03.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
841201	20.03.2007	< 0.01	0.02	< 0.01	< 0.027	0.01	58.00				
40787	20.03.2007	0.01	0.01	< 0.01	< 0.027	0.01	48.30				
40789	20.03.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	54.40				
822921	22.03.2007	0.02	0.01	0.04	< 0.027	< 0.046	84.60				
40780	22.03.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	46.00				
40782	22.03.2007	< 0.01	0.01	< 0.01	< 0.027	0.01	59.30				
873441	23.03.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	38.90				
967271	23.03.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	152.70				
820551	23.03.2007	0.46	0.41	0.06	0.09	0.05	61.10				
20219	11.04.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	14.30	2.07	365	6.1	293
20220	11.04.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	21.90	1.08	312	6.1	316
20230	12.04.2007	0.09	0.05	0.03	0.14	< 0.046	22.10	7.07	593	7.1	243

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20233	12.04.2007	0.09	0.05	< 0.01	0.17	0.02	108.00	7.45	669	6.9	243
873011	12.04.2007	0.04	0.06	< 0.01	< 0.027	< 0.046	79.10	5.45	725	6.7	267
1691	13.04.2007	0.14	0.11	< 0.01	< 0.027	< 0.046	65.70	6.32	679	6.8	240
873051	13.04.2007	0.17	0.12	< 0.01	< 0.027	0.02	68.00	6.06	681	6.8	236
20111	17.04.2007	0.14	0.11	< 0.01	< 0.027	0.03	64.70	6.80	722	6.8	229
20251	17.04.2007	0.01	0.03	< 0.01	< 0.027	< 0.046	71.50	3.81	653	6.5	231
20266	17.04.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	71.80	2.54	678	6.6	233
20267	17.04.2007	< 0.01	0.1	< 0.01	< 0.027	< 0.046	65.20	6.06	622	6.8	236
100390	18.04.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	22.80	4.28		6.5	236
100392	18.04.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	22.30	4.34		6.5	237
868921	23.04.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
822921	26.04.2007	0.02	< 0.01	< 0.01	< 0.027	< 0.046	88.10				
841201	26.04.2007	< 0.01	0.02	< 0.01	< 0.027	< 0.046	58.00				
40787	26.04.2007	< 0.01	0.02	< 0.01	< 0.027	< 0.046	46.50				
40789	26.04.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	53.10				
40780	27.04.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	44.70				
40782	27.04.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	59.80				
868921	15.05.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
873441	18.05.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	26.90				
967271	18.05.2007	0.19	0.13	0.02	0.03	0.02	104.50				
841201	21.05.2007	< 0.01	0.03	< 0.01	< 0.027	< 0.046	58.40				
40780	21.05.2007	< 0.01	0.02	< 0.01	< 0.027	< 0.046	46.00				
40782	21.05.2007	< 0.01	0.02	< 0.01	< 0.027	< 0.046	60.60				
40787	21.05.2007	< 0.01	0.02	< 0.01	< 0.027	< 0.046	46.90				
40789	21.05.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	53.10				
1691	21.05.2007	0.13	0.12	< 0.01	< 0.027	0.02	70.90		742	6.9	230
20111	21.05.2007	0.03	0.05	< 0.01	< 0.027	0.02	62.70		776	6.9	220
20251	21.05.2007	0.02	0.04	< 0.01	< 0.027	0.02	72.50		728	6.6	242
20266	21.05.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	45.20		679	6.4	244
20267	21.05.2007	0.04	0.06	< 0.01	< 0.027	0.02	63.60		641	7.1	216
822921	22.05.2007	0.03	0.03	0.04	< 0.027	< 0.046	88.10				
820551	22.05.2007	0.44	0.48	0.17	0.1	0.06	64.20				
100390	23.05.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	37.80			6.7	290
20230	23.05.2007	0.1	0.06	0.13	0.17	0.03	2.06		612	7.5	203
100392	23.05.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	43.00			6.6	283
20233	25.05.2007	0.11	0.08	0.11	0.21	0.04	67.40		689	6.8	255
873011	25.05.2007	0.1	0.1	< 0.01	< 0.027	0.02	92.50		732		
20219	29.05.2007	0.02	0.04	< 0.01	< 0.027	< 0.046	5.45		381	6.4	238
20220	29.05.2007	0.02	0.02	< 0.01	< 0.027	< 0.046	26.50		333	6.2	242
967271	19.06.2007	0.2	0.11	0.04	< 0.027	0.02	98.70				
40780	19.06.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	44.70				
40782	19.06.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	60.60				

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
820551	19.06.2007	0.43	0.45	0.15	0.1	0.05	63.30				
868921	21.06.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
873441	22.06.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	22.60				
822921	22.06.2007	0.02	0.01	< 0.01	< 0.027	< 0.046	87.70				
841201	22.06.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	58.40				
40787	22.06.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	46.90				
40789	22.06.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	54.00				
868921	23.07.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
40780	25.07.2007	0.01	0.01	< 0.01	< 0.027	< 0.046	47.80				
40782	25.07.2007	0.01	0.01	< 0.01	< 0.027	0.01	62.00				
841201	26.07.2007	< 0.01	0.02	< 0.01	< 0.027	0.02	58.90				
40787	26.07.2007	0.01	0.02	< 0.01	< 0.027	0.01	48.30				
40789	26.07.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	53.60				
820551	26.07.2007	0.41	0.4	< 0.01	0.1	0.06	63.70				
873441	27.07.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	20.80				
822921	27.07.2007	0.03	0.01	0.01	< 0.027	< 0.046	86.80				
967271	27.07.2007	0.21	0.12	0.04	< 0.027	0.03	95.60				
1691	03.08.2007	0.17	0.16	< 0.01	< 0.027	0.02	69.90		736	7.2	220
20111	03.08.2007	0.04	0.07	< 0.01	< 0.027	< 0.046	60.00		729	7.3	226
20251	03.08.2007	0.02	0.06	0.03	< 0.027	< 0.046	73.40		636	7.0	245
20266	03.08.2007	< 0.01	< 0.01	0.09	< 0.027	< 0.046	43.50		663	6.8	221
20267	03.08.2007	0.03	0.05	< 0.01	< 0.027	< 0.046	61.50		624	7.3	237
873011	10.08.2007	0.07	0.08	0.05	< 0.027	< 0.046	89.70		739		
100390	13.08.2007	< 0.01	0.02	< 0.01	< 0.027	< 0.046	31.90			6.7	221
20219	13.08.2007	0.02	0.05	0.04	< 0.027	< 0.046	19.00		378	6.3	226
20220	13.08.2007	0.02	0.04	0.01	< 0.027	< 0.046	20.80		333	6.4	161
20233	13.08.2007	0.13	0.09	0.13	0.28	0.03	63.00		681	6.9	158
100392	13.08.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	20.40			6.7	222
20230	15.08.2007	0.05	0.05	0.08	0.08	< 0.046	0.61		615	7.6	249
873051	15.08.2007	0.2	0.23	< 0.01	< 0.027	0.02	71.10		679		
868921	22.08.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
841201	24.08.2007	< 0.01	0.03	< 0.01	< 0.027	< 0.046	58.90				
40787	24.08.2007	< 0.01	0.02	< 0.01	< 0.027	< 0.046	47.40				
40789	24.08.2007	< 0.01	0.02	< 0.01	< 0.027	< 0.046	53.10				
873441	31.08.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	17.60				
822921	31.08.2007	< 0.01	0.01	0.02	< 0.027	< 0.046	88.10				
967271	31.08.2007	0.28	0.19	0.04	0.03	0.02	98.30				
40780	31.08.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	46.00				
40782	31.08.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	61.10				
820551	31.08.2007	0.47	0.57	0.19	0.12	0.06	63.70				
20111	20.09.2007	0.04	0.05	< 0.01	< 0.027	0.01	58.70		774		
20230	20.09.2007	0.12	0.04	0.13	0.17	0.02	53.00		582		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
-		µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20233	20.09.2007	0.12	0.06	0.11	0.23	0.03	66.30		659		
20251	20.09.2007	0.02	0.02	0.04	< 0.027	< 0.046	71.60		626		
20266	20.09.2007	< 0.01	< 0.01	0.04	< 0.027	< 0.046	50.20		681		
20267	20.09.2007	0.04	0.06	< 0.01	< 0.027	< 0.046	60.30		638		
873011	20.09.2007	0.07	0.06	0.04	< 0.027	0.01	88.30		711		
1691	24.09.2007	0.17	0.12	< 0.01	< 0.027	0.03	74.90		717		
20219	24.09.2007	0.02	0.02	0.04	< 0.027	< 0.046	12.90		383		
20220	24.09.2007	0.02	0.02	0.04	< 0.027	< 0.046	24.00		311		
873051	24.09.2007	0.24	0.14	< 0.01	< 0.027	0.03	72.70		768		
100390	25.09.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	19.10				
967271	25.09.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	93.80				
40780	25.09.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
40782	25.09.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	61.10				
40787	25.09.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	47.40				
100392	25.09.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	17.60				
873441	26.09.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	15.40				
822921	26.09.2007	0.02	0.01	0.04	< 0.027	< 0.046	87.20				
40789	26.09.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	49.60				
820551	26.09.2007	0.51	0.44	0.16	0.11	0.06	62.40				
868921	27.09.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	5.60				
841201	28.09.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046	58.40				
1691	12.10.2007	0.14	0.12	< 0.01	< 0.027	0.03	68.60		697		
100390	13.10.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	45.70				
100392	13.10.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	73.80				
20230	15.10.2007	0.07	0.08	0.1	< 0.027	0.02	57.70		581		
20233	15.10.2007	0.11	0.06	0.1	0.21	0.04	66.90		682		
873011	15.10.2007	0.05	0.06	0.04	< 0.027	0.02	89.90		717		
873051	15.10.2007	0.19	0.15	< 0.01	< 0.027	0.03	70.10		737		
20111	16.10.2007	0.14	0.13	< 0.01	< 0.027	0.03	69.80		768		
20219	16.10.2007	0.03	0.03	0.02	< 0.027	< 0.046	15.90		368		
20220	16.10.2007	0.03	0.03	0.02	< 0.027	< 0.046	26.00		302		
20267	16.10.2007	0.14	0.12	< 0.01	< 0.027	0.03	69.70		642		
868921	22.10.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	0.00				
20251	23.10.2007	0.03	0.03	0.02	< 0.027	0.02	71.10		631		
20266	23.10.2007	< 0.01	< 0.01	0.06	< 0.027	< 0.046	47.70		678		
40780	24.10.2007	0.01	0.01	< 0.01	< 0.027	< 0.046	45.20				
40782	24.10.2007	0.01	0.01	< 0.01	< 0.027	0.01	59.30				
40853	24.10.2007	0.06	0.04	0.03	0.04	0.02					
40712	24.10.2007	0.12	0.07	0.14	0.14	0.03					
841201	25.10.2007	< 0.01	0.02	< 0.01	< 0.027	0.01	58.40				
40787	25.10.2007	0.01	0.02	< 0.01	< 0.027	< 0.046	45.60				
40789	25.10.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	52.20				

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
873441	26.10.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	17.60				
822921	26.10.2007	0.03	0.02	0.04	< 0.027	< 0.046	88.50				
967271	26.10.2007	0.22	0.14	0.04	< 0.027	0.03	97.80				
873441	12.11.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
820551	12.11.2007	0.4	0.46	0.17	0.09	0.06					
822921	13.11.2007	0.02	0.01	0.01	< 0.027	< 0.046					
40780	13.11.2007	0.01	0.01	0.01	< 0.027	< 0.046					
40782	13.11.2007	< 0.01	0.01	0.01	< 0.027	< 0.046					
40787	13.11.2007	0.01	0.02	< 0.01	< 0.027	< 0.046					
868921	13.11.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
841201	14.11.2007	< 0.01	0.02	< 0.01	< 0.027	< 0.046					
40789	14.11.2007	< 0.01	0.01	< 0.01	< 0.027	< 0.046					
1691	20.11.2007	0.14	0.16	< 0.01	< 0.027	0.03	70.70		702		
20111	20.11.2007	0.14	0.12	< 0.01	< 0.027	0.03	70.70		760		
20251	20.11.2007	0.02	0.03	< 0.01	< 0.027	0.01	65.30		642		
20266	20.11.2007	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	47.30		682		
20267	20.11.2007	0.12	0.09	< 0.01	< 0.027	0.02	68.20		654		
20219	21.11.2007	0.02	0.03	< 0.01	< 0.027	< 0.046	15.60		387		
20220	21.11.2007	0.02	0.03	0.04	< 0.027	< 0.046	22.70		348		
873011	21.11.2007	0.06	0.06	< 0.01	< 0.027	0.02	22.30		728		
20233	22.11.2007	0.1	0.05	0.09	0.19	0.03	69.00		670		
873051	22.11.2007	0.18	0.12	< 0.01	< 0.027	0.03	72.70		717		
868921	14.01.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
841201	15.01.2008	0.01	0.03	< 0.01	< 0.027	0.01					
40782	15.01.2008	0.01	< 0.01	< 0.01	< 0.027	0.01					
40780	16.01.2008	0.02	0.02	< 0.01	< 0.027	< 0.046					
40787	16.01.2008	0.02	0.03	< 0.01	< 0.027	0.01					
40789	16.01.2008	0.01	0.02	< 0.01	< 0.027	< 0.046					
873441	17.01.2008	< 0.01	0.03	< 0.01	< 0.027	< 0.046					
822921	17.01.2008	0.03	0.02	0.04	< 0.027	< 0.046					
820551	17.01.2008	0.47	0.45	< 0.01	0.11	0.08					
20111	22.01.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	47.60	0.00	766	6.4	203
20251	22.01.2008	0.03	0.04	0.04	< 0.027	0.02	71.80	0.00	642	6.6	203
20266	22.01.2008	0.03	0.04	0.01	< 0.027	< 0.046	72.60	0.00	689	6.6	191
20267	22.01.2008	0.05	0.06	< 0.01	< 0.027	< 0.046	56.30		638		
1691	24.01.2008	0.29	0.22	< 0.01	< 0.027	< 0.046	72.90	0.00	629	6.9	217
20230	24.01.2008	0.11	0.06	0.13	0.15	0.03	51.50	0.00	585	6.9	274
20233	24.01.2008	0.13	0.07	0.1	0.22	0.04	66.10	0.25	681	6.5	245
873051	24.01.2008	0.22	0.14	< 0.01	< 0.027	0.04	67.50	0.00	642	6.9	172
20219	25.01.2008	0.03	0.038	0.04	< 0.027	0.01	39.10	0.00	428	7.0	269
20220	25.01.2008	0.03	0.04	0.02	< 0.027	< 0.046	87.40	0.00	299	6.2	254
873011	25.01.2008	0.11	0.1	0.04	< 0.027	< 0.046	90.10	0.00	664	6.7	270

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
868921	07.02.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
40782	08.02.2008	0.01	< 0.01	< 0.01	< 0.027	0.01					
873441	12.02.2008	< 0.01	0.05	< 0.01	< 0.027	< 0.046					
822921	12.02.2008	0.03	0.01	0.01	< 0.027	< 0.046					
820551	12.02.2008	0.42	0.47	0.17	0.1	0.07					
1691	12.02.2008	0.09	0.11	< 0.01	< 0.027	0.03		48.27	627		
20111	12.02.2008	0.07	0.09	< 0.01	< 0.027	0.04	60.30	2.62	777		
20267	12.02.2008	0.09	0.1	< 0.01	< 0.027	0.02	68.90	3.27	642		
873011	12.02.2008	0.04	0.05	< 0.01	< 0.027	0.02	87.80	9.70	675		
841201	13.02.2008	< 0.01	0.01	< 0.01	< 0.027	0.01					
40787	13.02.2008	0.03	0.04	< 0.01	< 0.027	0.02					
40789	13.02.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
20219	13.02.2008	0.02	0.03	0.02	< 0.027	< 0.046	24.40		424		
20220	13.02.2008	0.02	0.03	< 0.01	< 0.027	< 0.046	8.38		295		
20251	13.02.2008	0.03	0.038	0.04	< 0.027	0.03	73.60		667		
20266	13.02.2008	< 0.01	< 0.01	0.08	< 0.027	< 0.046	61.90	2.05	701		
20230	18.02.2008	0.11	0.04	0.15	0.12	< 0.046	52.20	1.72	581		
20233	18.02.2008	0.12	0.06	0.12	0.19	0.04	70.80	2.11	677		
873051	19.02.2008	0.16	0.11	< 0.01	< 0.027	0.03		2.78	639		
868921	17.03.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
1691	18.03.2008	0.17	0.13	< 0.01	< 0.027	0.03		2.35	638		
20111	18.03.2008	0.15	0.11	< 0.01	< 0.027	0.02	71.10		758		
20251	18.03.2008	< 0.01	< 0.01	< 0.01	< 0.027	0.03	68.10	3.49	662		
20266	18.03.2008	0.08	0.08	0.05	< 0.027	0.02	28.80	2.33	703		
20267	18.03.2008	0.14	0.09	< 0.01	< 0.027	0.02	71.00	17.80	630		
822921	20.03.2008	0.02	0.01	0.02	< 0.027	< 0.046					
40782	20.03.2008	< 0.01	0.01	< 0.01	< 0.027	< 0.046					
40787	25.03.2008	< 0.01	0.02	0.04	< 0.027	< 0.046					
40789	25.03.2008	< 0.01	0.01	0.02	< 0.027	< 0.046					
20219	25.03.2008	0.02	0.03	0.02	< 0.027	< 0.046	27.10	4.14	412		
20220	25.03.2008	0.02	0.03	0.03	< 0.027	< 0.046	20.50	2.16	282		
820551	26.03.2008	0.43	0.43	0.16	0.09	0.06					
20230	26.03.2008	0.12	0.05	0.19	0.18	0.02	52.80	1.53	549		
20233	26.03.2008	0.12	0.06	0.13	0.23	0.03		1.85	666		
873011	26.03.2008	0.06	0.06	< 0.01	< 0.027	0.01		2.17	639		
873051	26.03.2008	0.19	0.12	< 0.01	< 0.027	0.02	72.40	2.93	621		
1691	03.04.2008	0.13	0.11	< 0.01	< 0.027	0.02		4.44	628		
20111	03.04.2008	0.12	0.12	< 0.01	< 0.027	0.02		4.39	782		
20267	03.04.2008	0.13	0.11	< 0.01	< 0.027	0.02		39.92	638		
20219	08.04.2008	0.02	0.02	< 0.01	< 0.027	< 0.046		3.85	408		
20220	08.04.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046		1.78	296		
20251	09.04.2008	0.02	0.02	0.04	< 0.027	< 0.046		8.84	673		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
-		µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20266	09.04.2008	< 0.01	< 0.01	0.05	< 0.027	< 0.046			715		
20233	10.04.2008	0.1	0.07	0.1	0.21	0.03			678		
873011	10.04.2008	0.05	0.05	< 0.01	< 0.027	0.01			641		
868921	11.04.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
40782	15.04.2008	< 0.01	0.01	< 0.01	< 0.027	< 0.046					
820551	15.04.2008	0.45	0.46	0.14	0.1	0.06					
873441	16.04.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
822921	16.04.2008	0.02	0.01	0.04	< 0.027	< 0.046					
841201	17.04.2008	< 0.01	0.01	< 0.01	< 0.027	< 0.046					
40787	17.04.2008	< 0.01	0.02	< 0.01	< 0.027	< 0.046					
40789	17.04.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
868921	07.05.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
873441	09.05.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
967271	09.05.2008	0.07	0.05	< 0.01	< 0.027	< 0.046					
40780	09.05.2008	0.01	0.01	< 0.01	< 0.027	< 0.046					
40782	13.05.2008	0.01	0.02	< 0.01	< 0.027	0.01					
820551	13.05.2008	0.43	0.52	0.17	0.11	0.07					
822921	15.05.2008	0.03	0.02	0.02	< 0.027	< 0.046					
841201	15.05.2008	< 0.01	0.03	< 0.01	< 0.027	0.02					
40787	15.05.2008	0.02	0.02	< 0.01	< 0.027	0.01					
40789	15.05.2008	0.01	0.01	< 0.01	< 0.027	< 0.046					
1691	21.05.2008	0.07	0.06	< 0.01	< 0.027	0.02		3.36	672		
20111	21.05.2008	0.06	0.05	< 0.01	< 0.027	0.02		22.16	776		
20220	21.05.2008	0.02	0.02	< 0.01	< 0.027	< 0.046		3.09	303		
20251	21.05.2008	0.02	0.02	< 0.01	< 0.027	0.01		2.90	652		
20266	21.05.2008	< 0.01	< 0.01	0.04	< 0.027	< 0.046		11.65	706		
20267	21.05.2008	0.14	0.11	< 0.01	< 0.027	0.03		2.59	641		
873441	25.05.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
841201	25.05.2008	< 0.01	0.02	< 0.01	< 0.027	< 0.046					
100390	26.05.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
20219	26.05.2008	0.02	0.02	< 0.01	< 0.027	< 0.046		15.09	399		
20230	28.05.2008	0.09	0.05	0.13	0.14	0.03			579		
20233	28.05.2008	0.04	0.03	0.03	0.07	0.02		5.49	684		
873051	28.05.2008	0.16	0.11	< 0.01	< 0.027	0.03		17.86	632		
873011	29.05.2008	0.06	0.06	< 0.01	< 0.027	0.03		6.90	654		
1691	16.06.2008	0.13	0.11	< 0.01	< 0.027	0.03			658		
20111	16.06.2008	0.13	0.14	< 0.01	< 0.027	0.03			758		
20267	16.06.2008	0.13	0.11	< 0.01	< 0.027	0.03			640		
20219	17.06.2008	0.03	0.04	0.03	< 0.027	< 0.046			412		
20220	17.06.2008	0.03	0.038	0.03	< 0.027	0.02			288		
20230	20.06.2008	0.09	0.05	0.13	0.14	0.03			591		
20251	20.06.2008	0.03	0.04	0.03	< 0.027	0.02			666		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20266	20.06.2008	< 0.01	< 0.01	0.1	< 0.027	< 0.046			725		
100390	24.06.2008	0.01	< 0.01	< 0.01	< 0.027	< 0.046					
20233	24.06.2008	0.1	0.07	0.11	0.18	0.04			689		
873011	26.06.2008	0.06	0.06	0.04	< 0.027	0.03			676		
873051	26.06.2008	0.16	0.12	0.02	< 0.027	0.03			651		
20230	19.08.2008	0.09	0.05	0.11	0.14	0.03			621		
20251	19.08.2008	0.03	0.03	0.02	< 0.027	0.02			718		
20266	19.08.2008	0.02	0.038	0.05	< 0.027	0.01			714		
20233	20.08.2008	< 0.01	0.06	0.09	0.16	0.04			708		
873011	20.08.2008	0.05	0.05	0.04	< 0.027	0.02			743		
1691	21.08.2008	0.13	0.1	< 0.01	< 0.027	0.03			688		
20111	21.08.2008	0.12	0.11	< 0.01	< 0.027	0.03			771		
20267	21.08.2008	0.12	0.1	< 0.01	< 0.027	0.03			646		
20219	26.08.2008	0.04	0.05	0.03	< 0.027	0.01			408		
20220	26.08.2008	0.04	0.04	0.04	< 0.027	< 0.046			295		
100390	27.08.2008	0.01	< 0.01	< 0.01	< 0.027	< 0.046					
873051	27.08.2008	0.17	0.13	0.04	< 0.027	0.03			919		
1691	16.09.2008	0.12	0.11	< 0.01	< 0.027	0.03			672		
20111	16.09.2008	0.12	0.1	< 0.01	< 0.027	0.03			766		
20267	16.09.2008	0.13	0.11	< 0.01	< 0.027	0.03			644		
20230	22.09.2008	0.1	0.06	0.06	0.16	0.04					
20233	22.09.2008	0.1	0.06	0.05	0.17	0.04					
873051	22.09.2008	0.19	0.14	< 0.01	< 0.027	0.04					
20219	23.09.2008	0.04	0.04	0.04	< 0.027	< 0.046					
20220	23.09.2008	0.05	0.038	0.04	< 0.027	< 0.046					
20251	23.09.2008	0.06	0.06	0.04	< 0.027	0.02					
20266	23.09.2008	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046					
100390	25.09.2008	0.01	< 0.01	< 0.01	< 0.027	< 0.046					
873011	25.09.2008	0.03	0.03	0.04	< 0.027	0.02					
20219	17.10.2008						27.70	2.31	491		
20220	17.10.2008						44.00	2.29	474		
20267	20.11.2008						41.30	3.94			
20111	20.11.2008						73.90	3.20			
873051	20.11.2008						74.10	3.06	938		
1691	24.11.2008						77.00	2.81	922		
873011	24.11.2008						79.50	3.50	916		
20266	26.11.2008						64.70	3.30	944		
20230	26.11.2008						61.90	2.61	829		
20233	26.11.2008						67.70	3.10	946		
20251	26.11.2008						77.40	4.95	858		
20219	11.12.2008	0.02	0.038	0.04	< 0.027	< 0.046	29.60	3.11	526		
20220	11.12.2008	< 0.01	0.038	0.04	< 0.027	< 0.046	35.40	1.99	448		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20266	11.12.2008	< 0.01	0.01	< 0.01	< 0.027	< 0.046	64.40	3.05	945		
20230	15.12.2008						62.40	9.14	829		
20233	15.12.2008						71.70	2.29	942		
20251	15.12.2008	0.02	0.01	< 0.01	< 0.027	< 0.046	77.20	2.53	855		
1691	16.12.2008	0.18	0.14	< 0.01	< 0.027	0.03	76.40	15.57	923		
873051	16.12.2008	0.25	0.17	< 0.01	< 0.027	0.03	74.10	4.57	941		
820551	17.12.2008	0.45	0.54	0.09	0.11	0.07					
20111	17.12.2008	0.04	0.05	< 0.01	< 0.027	0.02	57.70	20.46	975		
20267	17.12.2008	0.01	< 0.01	< 0.01	0.03	< 0.046	42.00	5.60	749		
873011	17.12.2008						79.10	5.66	914		
20219	19.01.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	32.30	2.09	576		
20220	19.01.2009	< 0.01	< 0.01	0.02	< 0.027	< 0.046	31.70	2.70	439		
20251	19.01.2009	0.02	0.02	0.01	< 0.027	< 0.046	78.90	28.01	852		
20266	19.01.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	67.70	6.17	945		
20230	20.01.2009	0.08	0.04	0.13	0.13	0.02	66.60	2.44	839		
20233	20.01.2009	0.08	0.04	0.09	0.16	0.02	75.40	10.79	948		
873011	20.01.2009	0.04	0.04	< 0.01	< 0.027	< 0.046	82.60	15.91	917		
873051	20.01.2009	0.17	0.12	< 0.01	< 0.027	0.02	76.50	11.39	952		
820551	28.01.2009	0.31	0.36	0.11	0.13	0.05					
1691	28.01.2009	0.12	0.1	< 0.01	< 0.027	0.02	78.40	1.88	915		
20111	28.01.2009	0.04	0.04	< 0.01	< 0.027	0.02	60.20	2.08	974		
20267	28.01.2009	0.01	0.01	0.01	< 0.027	< 0.046	42.40	2.40	752		
820551	17.02.2009	0.41	0.45	0.14	0.1	0.06					
20219	17.02.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	31.10	1.88	575		
20220	17.02.2009	< 0.01	0.038	0.02	< 0.027	< 0.046	31.30	1.71	459		
20251	17.02.2009	0.02	0.02	< 0.01	< 0.027	< 0.046	75.30	1.69	854		
20266	17.02.2009	0.01	0.02	< 0.01	< 0.027	< 0.046	66.00	1.89	830		
20230	18.02.2009	0.11	0.06	0.17	0.17	0.03	64.60	6.88	837		
20233	18.02.2009	0.09	0.05	0.11	0.18	0.02	72.70	2.35	949		
873011	18.02.2009	0.06	0.06	< 0.01	< 0.027	0.01	79.30	2.27	913		
873051	18.02.2009	0.18	0.13	< 0.01	< 0.027	0.02	73.70	1.94	940		
1691	20.02.2009	0.12	0.1	< 0.01	< 0.027	< 0.046	71.50	2.16	912		
20111	20.02.2009	0.03	0.04	< 0.01	< 0.027	0.01	58.40	2.00	976		
20267	20.02.2009	0.01	0.038	0.04	< 0.027	< 0.046	37.80	2.09	754		
20219	16.03.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	36.50	2.40	560		
20220	16.03.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	32.40	3.04	462		
20230	16.03.2009	0.1	0.05	0.14	0.15	< 0.046	66.70	3.95	839		
20251	16.03.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	80.10	2.53	854		
873051	16.03.2009	0.19	0.13	< 0.01	< 0.027	< 0.046	77.00	2.07	957		
820551	18.03.2009	0.33	0.4	0.12	0.09	0.05					
1691	18.03.2009	0.14	0.11	< 0.01	< 0.027	< 0.046	75.30	2.58	913		
20233	18.03.2009	0.11	0.05	< 0.01	0.2	< 0.046	73.30	1.79	942		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20266	18.03.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	66.80	1.87	947		
873011	18.03.2009	0.05	0.05	< 0.01	< 0.027	< 0.046	79.70	2.57	920		
20111	19.03.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	60.40	2.46	978		
20267	19.03.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	48.20	2.04	752		
820551	16.04.2009	0.41	0.43	0.13	0.09	0.05			862		
20219	16.04.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	42.30	2.25	590		
20220	16.04.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	38.30	1.55	954		
20230	16.04.2009	0.09	0.06	0.11	0.13	< 0.046	63.50	4.14	825		
20251	16.04.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	78.40	1.80			
20266	16.04.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	67.40	2.12	945		
1691	20.04.2009	0.14	0.11	< 0.01	< 0.027	< 0.046	74.40	3.91	905		
20111	20.04.2009	< 0.01	0.05	< 0.01	< 0.027	< 0.046	60.40	2.76	972		
20233	20.04.2009	0.08	0.05	< 0.01	0.13	< 0.046	72.90	2.31	945		
873011	20.04.2009	0.05	< 0.01	< 0.01	< 0.027	< 0.046	81.50	2.49	920		
20267	21.04.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	43.10	3.03	757		
873051	21.04.2009	0.18	0.13	< 0.01	< 0.027	< 0.046	75.10	3.13	952		
820551	25.05.2009	0.34	0.4	0.14	0.09	0.05					
1691	25.05.2009	0.11	0.08	< 0.01	< 0.027	< 0.046	75.60	8.55	906		
20219	25.05.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	28.20	5.40	487		
20220	25.05.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	44.30	17.73	454		
20230	25.05.2009	0.08	< 0.01	< 0.01	0.12	< 0.046	62.30	11.20	818		
20233	25.05.2009	0.09	0.05	< 0.01	0.15	< 0.046	71.40	22.10	938		
20251	25.05.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	78.70		850		
20266	25.05.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	68.40		946		
873011	25.05.2009	0.06	0.06	< 0.01	< 0.027	< 0.046	76.40	6.76	914		
873051	26.05.2009	0.16	0.11	< 0.01	< 0.027	< 0.046	75.60	6.29	941		
20111	27.05.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	59.90	5.60	975		
20267	27.05.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	34.80	5.64	760		
820551	15.06.2009	0.34	0.39	0.14	0.09	0.06					
20219	16.06.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	26.30	3.70	5.16		
20220	16.06.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	47.10	7.20	456		
20251	16.06.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	75.00	4.23	852		
20266	16.06.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	64.40	5.03	948		
20230	17.06.2009	0.08	< 0.01	0.14	0.14	< 0.046	60.20	3.98	815		
20233	17.06.2009	0.09	0.05	< 0.01	0.16	< 0.046	67.50	4.44	943		
873011	17.06.2009	0.05	0.05	< 0.01	< 0.027	< 0.046	77.00	4.98	24.6		
1691	18.06.2009	0.14	0.11	< 0.01	< 0.027	< 0.046	73.10	4.37	903		
20111	18.06.2009	< 0.01	0.05	< 0.01	< 0.027	< 0.046	57.20	5.77	971		
873051	18.06.2009	0.18	0.13	< 0.01	< 0.027	< 0.046	72.70	5.73	935		
20267	19.06.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	33.80		750		
20219	15.07.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	24.50	5.36	4.81		
20220	15.07.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	54.80	4.88	460		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20230	15.07.2009	0.08	< 0.01	0.12	0.14	< 0.046	62.70	8.19	826		
20233	15.07.2009	0.1	0.06	< 0.01	0.16	< 0.046	67.00	10.63	938		
20251	15.07.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	75.50	9.72	845		
20266	15.07.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	66.50	11.08	944		
873011	16.07.2009	0.09	0.09	< 0.01	< 0.027	< 0.046	78.40	7.88	907		
873051	16.07.2009	0.2	0.14	< 0.01	< 0.027	< 0.046	74.90	10.35	933		
1691	17.07.2009	0.17	0.13	< 0.01	< 0.027	< 0.046	74.40	7.39	899		
20111	17.07.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	58.50	8.85	973		
20267	17.07.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	31.60	10.32	756		
820551	23.07.2009	0.34	0.37	0.14	0.09	0.05					
1691	01.08.2009	0.12	0.09	< 0.01	< 0.027	< 0.046	74.60	9.17	903		
20111	01.08.2009	< 0.01	0.06	< 0.01	< 0.027	< 0.046	58.10	13.43	965		
20219	01.08.2009	< 0.01	0.09	< 0.01	< 0.027	< 0.046	19.20	7.62	441		
20220	01.08.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	57.30	6.80	473		
20230	01.08.2009	0.08	0.05	< 0.01	0.14	< 0.046	62.60	9.69	797		
20233	01.08.2009	0.08	0.05	< 0.01	0.15	< 0.046	64.10	15.17	920		
20251	01.08.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	74.90	11.58	840		
20266	01.08.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	65.80	12.28			
20267	01.08.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	29.70	12.76	758		
873051	01.08.2009	0.19	0.13	< 0.01	< 0.027	< 0.046	74.50	11.52	930		
873011	04.08.2009	0.06	0.06	< 0.01	< 0.027	< 0.046	77.60	13.82	903		
820551	28.08.2009	0.3	0.35	0.1	0.07	0.05					
20219	17.09.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	22.00	2.40	476		
20220	17.09.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	35.90	36.63	442		
20230	17.09.2009	0.1	0.05	0.12	0.16	< 0.046	64.50	1.47	829		
20251	17.09.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	71.10	11.10	842		
20266	17.09.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	66.10	1.47	944		
873051	17.09.2009	0.24	0.15	< 0.01	< 0.027	< 0.046	73.70	2.27	936		
1691	18.09.2009	0.17	0.12	< 0.01	< 0.027	< 0.046	73.60	2.05	904		
20111	18.09.2009	0.05	0.06	< 0.01	< 0.027	< 0.046	58.20	5.80	972		
20233	18.09.2009	0.1	0.06	< 0.01	0.17	< 0.046	63.30	1.45	918		
20267	18.09.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	31.70	0.84	750		
873011	18.09.2009	0.07	0.07	< 0.01	< 0.027	< 0.046	78.30		912		
820551	13.10.2009	0.38	0.4	0.16	0.1	0.07					
20219	14.10.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	23.90	1.47	485		
20220	14.10.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	26.70	44.00	420		
20230	14.10.2009	0.1	0.06	0.13	0.17	< 0.046	64.20	2.44	795		
20251	14.10.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	76.80	9.46	858		
20266	14.10.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	66.20		929		
873051	15.10.2009	0.25	0.17	< 0.01	< 0.027	< 0.046	73.40	8.43	942		
1691	20.10.2009	0.17	0.13	< 0.01	< 0.027	< 0.046	74.10	11.60	909		
20111	20.10.2009	0.06	0.06	< 0.01	< 0.027	< 0.046	57.80		979		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20267	20.10.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	33.30	5.93	754		
873011	20.10.2009	0.07	0.06	< 0.01	< 0.027	< 0.046	78.40		911		
20233	21.10.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	13.40		918		
20219	18.11.2009	< 0.01	< 0.01	0.29	< 0.027	< 0.046	20.80	6.90	511		
20220	18.11.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	23.00	9.42	418		
20251	18.11.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	63.70		795		
1691	19.11.2009	0.19	0.13	< 0.01	< 0.027	< 0.046	73.50		911		
20111	19.11.2009	0.06	0.06	< 0.01	< 0.027	< 0.046	57.80		968		
20230	19.11.2009	0.11	0.06	0.15	0.16	< 0.046	64.10		789		
20233	19.11.2009	0.1	0.06	< 0.01	0.16	< 0.046	62.10	11.30	912		
20266	19.11.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	66.20	3.28	942		
873011	19.11.2009	0.09	0.07	< 0.01	< 0.027	< 0.046	78.30	9.12	913		
873051	19.11.2009	0.24	0.16	< 0.01	< 0.027	< 0.046	73.80		940		
820551	20.11.2009	0.4	0.43	0.16	0.1	0.07					
20267	20.11.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	33.90		753		
820551	10.12.2009	0.36	0.41	0.13	0.09	0.06					
20220	13.12.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	22.20	10.35	427		
20219	14.12.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	25.00		499		
20251	15.12.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	75.00	12.66	845		
20266	15.12.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	66.30		934		
1691	16.12.2009	0.17	0.14	< 0.01	< 0.027	< 0.046	73.80		912		
20111	16.12.2009	0.05	0.06	< 0.01	< 0.027	< 0.046	58.60	2.75	968		
20230	16.12.2009	0.1	0.06	0.15	0.16	< 0.046	64.80	2.84			
20233	16.12.2009	0.1	0.07	< 0.01	0.16	< 0.046	61.70	12.32	914		
873011	16.12.2009	0.07	0.06	< 0.01	< 0.027	< 0.046	79.00	7.47	908		
20267	17.12.2009	< 0.01	< 0.01	< 0.01	< 0.027	< 0.046	33.00		767		
873051	17.12.2009	0.23	0.16	< 0.01	< 0.027	< 0.046	74.00		950		
20219	18.01.2010	< 0.05	0	< 0.05	< 0.05	< 0.05	28.30	1.52	515		
20220	18.01.2010	< 0.05	0	< 0.05	< 0.05	< 0.05	24.90	23.50	434		
20230	18.01.2010	0.08	0.05	0.13	0.16	< 0.05	66.40		835		
20251	18.01.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	76.50	1.72	837		
20266	18.01.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	67.80	1.35	912		
1691	20.01.2010	0.17	0.13	< 0.05	< 0.05	< 0.05	73.80		910		
20233	20.01.2010	0.09	0.06	< 0.05	0.16	< 0.05	62.10	4.43	916		
20267	20.01.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	30.30	1.68	872		
873011	20.01.2010	0.07	0.06	< 0.05	< 0.05	< 0.05	79.30		912		
873051	20.01.2010	0.21	0.15	< 0.05	< 0.05	< 0.05	74.70	1.20	962		
820551	21.01.2010	0.39	0.42	0.13	0.1	0.06					
20111	21.01.2010	0.05	0.06	< 0.05	< 0.05	< 0.05	58.80		974		
20219	18.02.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	32.60	1.54	587		
20220	18.02.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	26.40	1.11	580		
20251	18.02.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	76.80	1.26	646		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20266	18.02.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	67.10	1.35	944		
1691	19.02.2010	0.16	0.13	< 0.05	< 0.05	< 0.05	71.00	0.88	896		
20111	19.02.2010	< 0.05	0.06	< 0.05	< 0.05	< 0.05	58.00	1.37	967		
20230	19.02.2010	0.1	0.06	0.16	0.17	< 0.05	67.70	1.47	847		
20233	19.02.2010	0.09	0.06	< 0.05	0.06	< 0.05	61.30	1.52	905		
20267	19.02.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	31.30	1.35	734		
873011	19.02.2010	0.06	0.06	< 0.05	< 0.05	< 0.05	80.40	1.61	924		
873051	19.02.2010	0.21	0.14	< 0.05	< 0.05	< 0.05	76.70	1.62	941		
20219	16.03.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	36.60	1.39	589		
20220	16.03.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	27.40	0.87	428		
20251	16.03.2010	0.16	0.13	< 0.05	< 0.05	< 0.05	80.00	1.10	843		
20266	16.03.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	67.80	1.17	953		
1691	17.03.2010	0.16	0.13	< 0.05	< 0.05	< 0.05	73.80	0.85	912		
20111	17.03.2010	0.05	0.06	< 0.05	< 0.05	< 0.05	58.80	1.39	966		
20230	17.03.2010	0.11	0.06	0.14	0.15	0.05	67.60	0.95	847		
20233	17.03.2010	0.09	0.06	< 0.05	0.15	< 0.05	61.90	1.33	977		
873011	17.03.2010	0.07	0.06	< 0.05	< 0.05	< 0.05	82.60	1.41	926		
20267	18.03.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	39.50	1.20	783		
873051	18.03.2010	0.19	0.13	< 0.05	< 0.05	< 0.05	74.50	1.35	974		
20219	21.04.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	34.70	1.67	596		
20220	21.04.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	31.10	0.89	422		
20230	21.04.2010	0.1	0.06	0.12	0.15	< 0.05	68.50	1.09	843		
20233	21.04.2010	0.09	0.07	< 0.05	0.13	< 0.05	62.50	1.22	910		
20251	21.04.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	80.70	1.11	817		
20266	21.04.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	68.20	1.15	944		
1691	22.04.2010	0.16	0.14	< 0.05	< 0.05	< 0.05	74.60	1.42	908		
20267	22.04.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	31.90	1.39	761		
873011	22.04.2010	0.06	0.06	< 0.05	< 0.05	< 0.05	85.50	1.44	930		
873051	22.04.2010	0.2	0.13	< 0.05	< 0.05	< 0.05	75.20	1.56	970		
100390	22.04.2010								648		
1691	14.05.2010	0.17	0.13	< 0.05	< 0.05	< 0.05	73.60	2.33			
20251	16.05.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	83.30	1.56	647		
20219	18.05.2010	< 0.05	0.07	< 0.05	< 0.05	< 0.05	29.40	1.91			
20220	18.05.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	36.40	2.04	435		
20230	18.05.2010	0.1	0.06	0.13	0.15	< 0.05	66.70	1.11	781		
20266	18.05.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	67.90	1.81	932		
20111	19.05.2010	0.05	0.07	< 0.05	< 0.05	< 0.05	58.40	1.53			
20267	19.05.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	27.10	1.34			
20233	21.05.2010	0.09	0.08	< 0.05	0.13	< 0.05	58.30	1.35	898		
873011	21.05.2010	0.06	0.07	< 0.05	< 0.05	< 0.05	83.20	1.46	929		
873051	22.05.2010	0.2	0.14	< 0.05	< 0.05	< 0.05	74.60	1.67	965		
20219	18.06.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05		4.90	582		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
-		µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
1691	20.06.2010	0.16	0.15	< 0.05	< 0.05	< 0.05		2.23	891		
20230	20.06.2010	0.09	0.09	0.18	0.15	< 0.05		4.81	830		
20251	20.06.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05		3.50	663		
20266	20.06.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05		1.65	932		
873011	20.06.2010	0.06	0.07	< 0.05	< 0.05	< 0.05		1.65	908		
20111	21.06.2010	0.05	0.06	< 0.05	< 0.05	< 0.05		1.39	957		
100390	22.06.2010								665		
20267	22.06.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05		1.88	752		
20220	23.06.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05		1.57			
20233	24.06.2010	0.08	0.09	< 0.05	0.13	< 0.05		1.82			
873051	25.06.2010	0.2	0.16	< 0.05	< 0.05	< 0.05		1.46			
20219	23.07.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	21.20	1.81	564		
20220	23.07.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	41.70	0.92	436		
20230	23.07.2010	0.09	0.06	0.15	0.15	< 0.05	66.00	0.62	728		
20251	23.07.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	76.20	8.71			
20266	23.07.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	69.60	0.83	932		
100390	24.07.2010								641		
1691	24.07.2010	0.16	0.14	< 0.05	< 0.05	< 0.05	75.60	1.40	901		
20111	24.07.2010	0.05	0.06	< 0.05	< 0.05	< 0.05	59.60	0.94	951		
20233	24.07.2010	0.09	0.08	< 0.05	0.13	< 0.05	62.60	1.54	901		
20267	24.07.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29.30	2.11	756		
873011	24.07.2010	0.07	0.08	< 0.05	< 0.05	< 0.05	83.30	3.29	908		
873051	25.07.2010	0.21	0.16	< 0.05	< 0.05	< 0.05	77.40	11.66	950		
20219	24.08.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	16.40	1.18	427		
20220	24.08.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	27.40	0.73	458		
20230	24.08.2010	0.11	0.05	0.17	0.16	< 0.05	24.50	0.83	798		
20251	24.08.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	72.80	0.90	703		
20266	24.08.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	68.70	1.07	930		
20111	25.08.2010	0.05	0.06	< 0.05	< 0.05	< 0.05	58.20	0.94	957		
20233	25.08.2010	0.08	0.07	< 0.05	0.13	< 0.05	62.00	1.09	904		
873011	25.08.2010	0.07	0.06	< 0.05	< 0.05	< 0.05	83.70	0.99	904		
873051	25.08.2010	0.22	0.15	< 0.05	< 0.05	< 0.05	76.70	0.86	955		
100390	26.08.2010								661		
1691	26.08.2010	0.17	0.13	< 0.05	< 0.05	< 0.05	75.10	1.12	905		
20267	26.08.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	27.70	1.04	762		
20219	28.09.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23.20	1.18			
20220	28.09.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	19.60	0.77			
20233	28.09.2010	0.09	0.05	< 0.05	0.12	< 0.05	60.30	0.78			
1691	29.09.2010	0.17	0.11	< 0.05	< 0.05	< 0.05	73.90	0.83			
20230	29.09.2010	0.13	< 0.05	0.14	0.15	< 0.05	5.49	0.90			
20251	29.09.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	74.80	0.89			
20266	29.09.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	68.10	0.82			

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
873011	29.09.2010	0.08	0.05	< 0.05	< 0.05	< 0.05	82.60	1.07			
873051	29.09.2010	0.23	0.15	< 0.05	< 0.05	< 0.05	75.20	0.86			
20111	30.09.2010	0.05	0.06	< 0.05	< 0.05	< 0.05	57.50	0.87			
20267	30.09.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	28.00	0.68			
20219	25.10.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29.10	1.33			
20220	25.10.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	21.40	0.95			
20230	25.10.2010	0.07	0.07	< 0.05	< 0.05	< 0.05	5.95	1.05			
20233	25.10.2010	0.09	0.07	< 0.05	0.13	< 0.05	61.70	1.00			
20251	25.10.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	78.60	0.84			
20266	25.10.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	67.00	1.04			
873011	25.10.2010	0.07	0.07	< 0.05	< 0.05	< 0.05	83.30	1.02			
1691	26.10.2010	0.18	0.15	< 0.05	< 0.05	< 0.05	73.60	0.90			
20111	26.10.2010	0.05	0.07	< 0.05	< 0.05	< 0.05	57.10	1.00			
20267	26.10.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29.10	1.01			
873051	26.10.2010	0.24	0.17	< 0.05	< 0.05	< 0.05	74.20	0.91			
20219	11.11.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24.20	1.19	648		
20220	11.11.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24.50	0.79	652		
20230	11.11.2010	0.07	< 0.05	< 0.05	0.06	< 0.05	25.10	0.92	792		
20266	11.11.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	67.00	0.95	910		
1691	15.11.2010	0.13	< 0.05	< 0.05	< 0.05	< 0.05	71.90	1.44	897		
20111	15.11.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	56.50	1.05	951		
20251	15.11.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	77.90	0.85	807		
20267	15.11.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	26.40	1.16	808		
873011	15.11.2010	0.05	< 0.05	< 0.05	< 0.05	< 0.05	82.00	1.12	911		
20233	16.11.2010	0.06	< 0.05	< 0.05	0.05	< 0.05	62.80	0.87	902		
873051	16.11.2010	0.17	< 0.05	< 0.05	< 0.05	< 0.05	74.90	1.09	675		
20111	14.12.2010	0.05	0.06	< 0.05	< 0.05	< 0.05	56.40	0.98	950		
20219	14.12.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	33.10	1.26	540		
20220	14.12.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	18.30	1.09	428		
20230	14.12.2010	0.09	< 0.05	0.17	0.13	< 0.05	4.49	0.97	838		
20251	14.12.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	78.60	1.25	808		
20266	14.12.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	67.50	0.91	927		
1691	15.12.2010	0.15	0.12	< 0.05	< 0.05	< 0.05	74.00	0.97	907		
20233	15.12.2010	0.09	0.06	< 0.05	0.12	< 0.05	59.40	0.88	873		
20267	15.12.2010	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	30.10	0.98	770		
873011	15.12.2010	0.07	0.07	< 0.05	< 0.05	< 0.05	84.30	1.12	916		
873051	15.12.2010	0.19	0.13	< 0.05	< 0.05	< 0.05	74.90	1.03	970		
20230	18.01.2011	0.08	< 0.05	0.13	0.14	< 0.05	1.18	0.98	795		
1691	19.01.2011	0.14	0.12	< 0.05	< 0.05	< 0.05	68.20	1.23	571		
20111	19.01.2011	0.05	0.06	< 0.05	< 0.05	< 0.05	56.10	5.29	703		
20219	19.01.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	42.30	1.39	650		
20220	19.01.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	21.00	0.68	656		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20233	19.01.2011	0.08	0.06	< 0.05	0.13	< 0.05	86.30	2.79	904		
20267	19.01.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	39.10	0.87	550		
873011	19.01.2011	0.06	0.06	< 0.05	< 0.05	< 0.05	86.50	1.22	676		
873051	19.01.2011	0.19	0.12	< 0.05	< 0.05	< 0.05	73.60	1.46	656		
20251	20.01.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	66.40	1.03	704		
20266	20.01.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	62.60	1.04	930		
1691	01.02.2011	0.15	0.11	< 0.05	< 0.05	< 0.05	69.70	1.09	888		
20111	01.02.2011	0.05	0.06	< 0.05	< 0.05	< 0.05	54.40	11.57	948		
20219	01.02.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	48.90	1.09	533		
20220	01.02.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	21.00	0.89	807		
20230	01.02.2011	0.09	< 0.05	0.16	0.15	< 0.05	0.04	1.01	790		
20233	01.02.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	78.10	2.17	902		
20251	01.02.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	72.40	0.80	807		
20266	01.02.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	64.20	0.91	910		
20267	01.02.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	32.90	2.37	815		
873011	01.02.2011	0.06	0.06	< 0.05	< 0.05	< 0.05	91.70	1.02	909		
873051	01.02.2011	0.19	0.13	< 0.05	< 0.05	< 0.05	73.90	1.17	675		
1691	01.03.2011	0.16	0.12	< 0.05	< 0.05	< 0.05	74.50	3.22			
20111	01.03.2011	0.06	0.07	< 0.05	< 0.05	< 0.05	55.40	2.72			
20219	01.03.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	41.70	1.25			
20220	01.03.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29.90	3.27			
20230	01.03.2011	0.1	0.06	0.16	0.16	< 0.05	51.00	1.02			
20233	01.03.2011	0.09	0.07	< 0.05	0.15	< 0.05	62.10	1.06			
20251	01.03.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	76.30	1.46			
20266	01.03.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	68.20	0.89			
20267	01.03.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23.00	0.73			
873011	01.03.2011	0.06	0.06	< 0.05	< 0.05	< 0.05	90.70	0.98			
873051	01.03.2011	0.19	0.13	< 0.05	< 0.05	< 0.05	79.10	1.02			
20219	19.04.2011	0.05	< 0.05	< 0.05	< 0.05	< 0.05			627		
20220	19.04.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05			432		
20230	19.04.2011	0.1	0.06	0.15	0.15	< 0.05			908		
20251	19.04.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05			952		
20266	19.04.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05			974		
873051	19.04.2011	0.19	0.12	< 0.05	< 0.05	< 0.05			996		
1691	20.04.2011								898		
20111	20.04.2011	0.06	0.07	< 0.05	< 0.05	< 0.05			999		
20233	20.04.2011	0.09	0.06	< 0.05	0.14	< 0.05					
873011	20.04.2011	0.06	< 0.05	< 0.05	< 0.05	< 0.05			931		
20267	21.04.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05			778		
100390	26.04.2011								664		
20266	18.05.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	66.70	1.27	970		
20267	18.05.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	28.20	2.89	780		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
	-	µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
100390	18.05.2011						8.51	1.27	668		
873011	18.05.2011	0.1	0.08	< 0.05	< 0.05	< 0.05	86.30	1.33	930		
873051	18.05.2011	0.19	0.1	< 0.05	< 0.05	< 0.05	80.50	5.15	995		
20230	19.05.2011	0.1	0.07	0.18	0.16	0.05	70.40	0.94	908		
20233	19.05.2011	0.09	0.08	< 0.05	0.12	< 0.05	60.60	1.02	902		
20251	19.05.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	69.70	1.03	952		
1691	21.05.2011						79.30	1.33	897		
20111	21.05.2011	0.06	0.08	< 0.05	< 0.05	< 0.05	54.50	4.28	998		
20219	21.05.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	24.70	3.63	628		
20220	21.05.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	38.00	1.01	430		
1691	18.06.2011								881		
20111	18.06.2011	0.07	0.08	< 0.05	< 0.05	< 0.05			940		
20219	18.06.2011	0.05	< 0.05	< 0.05	< 0.05	< 0.05			504		
20220	18.06.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05			408		
20251	18.06.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05			1173		
20267	18.06.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05			748		
20230	20.06.2011	0.1	0.06	0.15	0.16	< 0.05			884		
20233	20.06.2011	0.1	0.07	< 0.05	0.1	< 0.05			893		
20266	20.06.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05			925		
100390	21.06.2011								663		
873011	21.06.2011	0.06	0.06	< 0.05	< 0.05	< 0.05			875		
873051	21.06.2011	0.21	0.13	< 0.05	< 0.05	< 0.05			916		
20230	18.07.2011	0.09	0.08	0.12	0.14	< 0.05	27.30	21.77	839		
20266	18.07.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	74.60	20.58	925		
100390	18.07.2011						12.60	4.82	680		
20111	20.07.2011	0.07	0.07	< 0.05	< 0.05	< 0.05	57.60	28.33	984		
20219	20.07.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	23.00	1.71	518		
20220	20.07.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	59.30	0.90	469		
20267	20.07.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	30.70	18.75	762		
1691	21.07.2011						80.10	19.38	878		
20233	21.07.2011	0.09	0.06	< 0.05	0.11	< 0.05	62.60	20.30	909		
20251	21.07.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	46.10	1.04	950		
873011	21.07.2011	0.07	0.06	< 0.05	< 0.05	< 0.05	83.00	18.70	889		
873051	21.07.2011	0.21	0.12	< 0.05	< 0.05	< 0.05	79.10	21.28	909		
20230	09.08.2011	0.1	0.06	0.12	0.13	< 0.05	42.00	8.89	839		
20233	09.08.2011	0.09	0.06	< 0.05	0.11	< 0.05	62.80	6.00	915		
20251	09.08.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	47.10	1.07	955		
873011	09.08.2011	0.07	0.06	< 0.05	< 0.05	< 0.05	81.40	5.35	890		
20111	10.08.2011	0.08	0.09	< 0.05	< 0.05	< 0.05	56.40	12.76	984		
20219	10.08.2011	0.05	< 0.05	< 0.05	< 0.05	< 0.05	20.80	1.88	510		
20220	10.08.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	45.90	1.17	470		
873051	10.08.2011	0.19	0.13	< 0.05	< 0.05	< 0.05	79.10	6.82	910		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
-		µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
1691	11.08.2011						80.30	8.23	870		
20266	11.08.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	64.60	8.26	910		
20267	11.08.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	29.40	6.76	775		
100390	15.08.2011						14.70	1.55	693		
20111	20.09.2011	0.06	0.07	< 0.05	< 0.05	< 0.05	60.10	14.58	998		
20220	20.09.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	32.50	1.14	432		
20230	20.09.2011	0.08	0.05	< 0.05	0.13	< 0.05	0.00	31.91	906		
20251	20.09.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	58.70	1.45	952		
20266	20.09.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	69.20	8.10	972		
20233	21.09.2011	< 0.05	< 0.05	< 0.05	0.06	< 0.05	56.70	5.44	902		
20267	21.09.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	36.00	3.38	778		
1691	22.09.2011						82.70	6.39	898		
873051	22.09.2011	0.13	0.13	< 0.05	< 0.05	< 0.05	84.50	9.02	996		
20219	23.09.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	27.30	2.00	629		
873011	23.09.2011	0.07	0.05	< 0.05	< 0.05	< 0.05	79.80	10.20	931		
100390	23.09.2011						20.80	2.71	667		
1691	18.10.2011						78.60	7.73	887		
20267	18.10.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	38.20	4.94	745		
873011	18.10.2011	0.07	0.06	< 0.05	< 0.05	< 0.05	80.50	7.06	879		
873051	18.10.2011	0.2	0.14	< 0.05	< 0.05	< 0.05	77.50	12.26	933		
20230	19.10.2011	0.09	0.07	0.14	0.15	< 0.05	73.00	0.66	871		
20233	19.10.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	63.50	6.59	853		
20251	19.10.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	58.30	1.35	958		
20266	19.10.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	66.40	9.43	934		
20111	20.10.2011	0.06	0.07	< 0.05	< 0.05	< 0.05	57.40	77.10	976		
20219	20.10.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	25.70	1.55	513		
20220	20.10.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	36.50	1.06	473		
20219	16.11.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	30.90	1.81	544		
20220	16.11.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	31.50	1.11	442		
20251	16.11.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	79.20	1.52	984		
873051	16.11.2011	0.21	0.13	< 0.05	< 0.05	< 0.05	77.40	7.95	934		
20230	21.11.2011	0.08	0.05	< 0.05	0.15	0.05	0.00	17.98	871		
20111	22.11.2011	0.06	0.07	< 0.05	< 0.05	< 0.05	59.00	14.84	958		
20233	22.11.2011	< 0.05	< 0.05	< 0.05	0.09	< 0.05	59.30	5.34	865		
20266	22.11.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	67.80	9.20	934		
873011	22.11.2011	0.07	0.07	< 0.05	< 0.05	< 0.05	81.60	7.13	877		
1691	23.11.2011						79.40	9.39	886		
20267	23.11.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	36.80	4.97	746		
1691	13.12.2011						80.40	6.69	884		
20219	13.12.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	27.70	1.66	543		
20220	13.12.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	21.90	1.13	448		
20111	14.12.2011	0.06	0.13	< 0.05	< 0.05	< 0.05	59.60	16.76	956		

OW	Date	Atrazine	DEA	DIA	Simazine	Propazine	Nitrate	DOC	EC	pH	Redox-Pot.
-		µg L^{-1}					mg l^{-1}		µS cm^{-1}	-	mV
20233	14.12.2011	0.11	< 0.05	< 0.05	0.13	< 0.05	63.40	4.75	980		
20267	14.12.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	34.70	4.66	765		
873011	14.12.2011	0.08	0.07	< 0.05	< 0.05	< 0.05	80.90	5.88	882		
873051	14.12.2011	0.22	0.14	< 0.05	< 0.05	< 0.05	78.80	8.56	943		
20230	15.12.2011	0.1	0.06	0.12	0.16	< 0.05	64.70	0.59	872		
20251	15.12.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	66.50	1.09	982		
20266	15.12.2011	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	67.90	7.79	932		

Table 14: Atrazine concentration trend anaysis for each observation well. Linear regression fits on atrazine concentration data were tested for significance by the F-test. The null hypothesis that the coefficient of determination of the linear regression fit is zero (no trend) is rejected for P-values smaller than 0.05 (for a singificance level α = 0.05) (increasing or decreasing trend).

Observation well	P-value	Trend direction
1691	0.000	increasing
20111	0.561	no trend
20218	n.d.[1]	no trend
20219	0.000	decreasing
20220	0.000	decreasing
20230	0.256	no trend
20232	n.d.	no trend
20233	0.000	decreasing
20250	n.d.	no trend
20251	0.007	decreasing
20254	n.d.	no trend
20266	0.003	decreasing
20267	0.001	decreasing
40712	0.201	no trend
40780	0.192	no trend
40782	0.028	increasing
40787	0.046	no trend
40789	n.d.	no trend
40853	0.175	no trend
100390	0.022	increasing
100392	n.d.	no trend
820551	0.221	no trend
822901	0.009	increasing
822921	0.397	no trend

841201	n.d.	no trend
868921	n.d.	no trend
873011	0.863	no trend
873051	0.000	increasing
873441	n.d.	no trend
927761	n.d.	no trend
927851	0.038	decreasing
927931	0.139	no trend
960361	0.173	no trend
967271	0.775	no trend
822951	0.002	decreasing
872121	0.036	increasing

[1]**n.d.: no data or data consisting of nonquantifiable values.**

Table 15: Times of sampling of particular observation wells used for monitoring the Zwischenscholle aquifer.

OW	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
1352											■		■									
1691										■	■	■	■		■	■	■	■	■	■	■	■
20111										■	■	■	■		■	■	■	■	■	■	■	■
20197										■		■	■									
20203												■	■									
20204										■		■	■									
20205										■	■	■	■									
20206												■	■									
20211	■									■	■		■									
20218										■		■	■									
20219										■		■	■		■	■	■	■	■	■	■	■
20220		■								■	■	■	■		■	■	■	■	■	■	■	■
20221		■																				
20224	■																					
20225	■																					
20226												■	■									
20228	■																					
20230	■											■	■		■	■	■	■	■	■	■	■
20231	■											■	■									
20232	■									■	■		■									
20233	■									■	■		■		■	■	■	■	■	■	■	■
20234	■																					
20235	■																					
20242										■	■		■									
20243											■											
20244										■	■		■									
20249										■	■	■	■									
20250	■									■		■	■									
20251	■											■	■		■	■	■	■	■	■	■	■
20254										■	■	■	■									
20255												■	■									
20266		■										■	■		■	■	■	■	■	■	■	■
20267		■								■	■	■	■		■	■	■	■	■	■	■	■
40712				■			■	■		■	■	■	■	■	■	■	■					
40780																■	■	■				
40782																■	■	■				
40787																■	■	■				
40789																■	■	■				
40853				■			■	■		■	■	■					■					
100390															■	■	■	■				

OW	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
100392																						
820551																						
822901																						
822921																						
841201																						
868921																						
870891																						
873011																						
873051																						
873441																						
927761																						
927851																						
927931																						
960191																						
960201																						
960361																						
967151																						
967271																						

Appendix B: Atrazine and 2-hydroxyatrazine soil residue analysis

Table 16: List of equipments.

Type	Product name	Manufacturer
ASE	Dionex ASE 2000	Thermo Scientific
Inductively coupled plasma optical emission spectrometry (ICP-OES)	TJA-IRIS-Intrpid	Thermo Scientific
Water Purifier	Milli-Q 185 Plus	Waters
Manual drill-probe (Bohrsonde)	Humax	Martin Burch AG
Carbon and Water Determination	RC 612	Leco
Laser Diffraction Particle Size Analyser	LS 13 320	Beckman Coulter
LC-MS/MS	Thermo Electron Model TSQ Quantum 2002	Thermo Scientific
LC-MS/MS: Autosampler	CTC HTC PAL	
LC-MS/MS: Software	Xcalibur Version 3.1	
LC-MS/MS: Column	PerfectSil Target ODS-3; 12,5 cm length, 2,1 mm inner diameter, 3 µm particle size	MZ Analysentechnik GmbH
LC-MS/MS: Pre-column	PerfectSil Target ODS-3; 2 cm length, 2,1 mm inner diameter	
Membran vacuum pump	MZ 2c	Vacuubrand GmbH&Co
pH-Electrode	SevenEasy	Mettler Toledo
Planetary mill	PM 400	Retsch
Precision balance	XP5003S Delta Range	Mettler Toledo
	XP6002S	
Rhönradmischer	Mini 80	J. Engelsmann AG
	Mini II	

Dry powder system for particle sizer	Dry Powder System, Tornado	Beckman Coulter
Vacuum chamber		Macherey-Nagel

Table 17: List of chemicals

Product name	**Purity**	**Manufacturer**
(D_5)-2-Hydroxyatrazine	97%	Dr. Ehrenstorfer GmbH
(D_5)-Atrazine	99%	Dr. Ehrenstorfer GmbH
Acetonitrile (ASE)	99,5%	Merck
Acetonitrile (LC-MS/MS)		Biosolve
Ammonium acetate (LC-MS/MS)		Merck
Atrazine	99%	Dr. Ehrenstorfer GmbH
$BaCl_2$		
$CaCl_2$-Dihydrat	99,5%, p.a.	Merck
Diatomaceous earth	100%	Thermo Scientific
Ethanol	99,9% für LC	
Hydroxyatrazine	10 ng/µL	Dr. Ehrenstorfer GmbH
Methanol	99,8%, p.a.	BDH Prolabo
$MgCl_2$		
Quarz	p.a.	Merck
Hydrochloric acid	37%, p.a.	Merck

Accelerated Solvent Extraction (ASE) and LC-MS/MS method validation

In Figure 16 and Figure 17, chromatograms of LC-MS/MS-analysis for the extracts using 100°C and 206.8 bar, atrazine peaks show a higher signal-to-noise ratio (20.8:1; atrazine peak height: 1250; background height: 60) and a higher atrazine peak area (5549; background area 200) compared to extracts using 135°C and 206.8 bar (signal-to-noise ratio: 10.8:1; atrazine peak height: 650; atrazine peak area: 3920; background height: 60, background area 200). The reduction of atrazine peak area and height can be explained by a quenching effect probably caused by an increased co-extraction of soil-matrix compounds using a higher extraction temperature of 135°C.

The chromatogram of Figure 18 shows the LC-MS/MS analysis for KS-B extracts with a gradient elution time of 35 minutes. In this case, for a low atrazine concentration the analyte does not differ from the background noise. Hence, quantification of the analyte is not possible. By extending the gradient elution time to 50 min (Figure 16 and Figure 17) signal quality improved distinctively, reduced the background noise by pulling apart peaks of soil compounds and made proper quantification possible in the low atrazine concentration range (LOQ = 0.01 ng mL^{-1} for atrazine and 2-hydroxyatrazine).

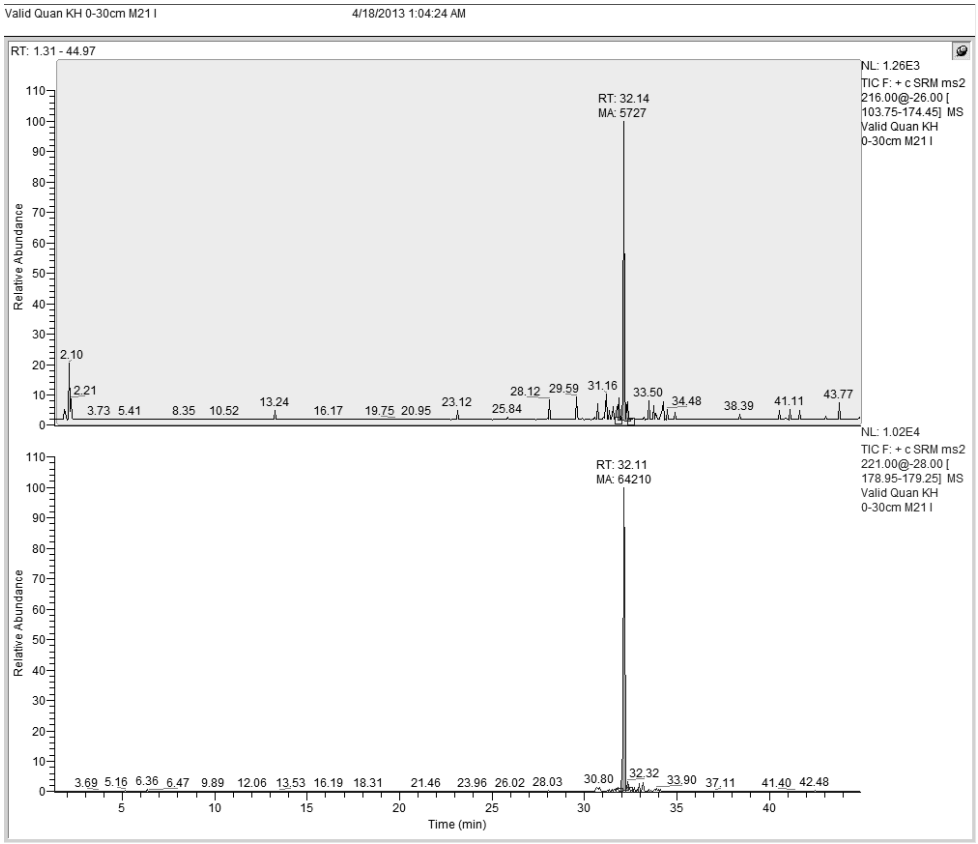

Figure 16: Top: Chromatogram of LC-MS/MS Analysis of extracts of Krauthausen Soil B (KS-B) using 100°C and 206.8 bar as ASE Parameters, with an atrazine retention time of 32.14 min. The signal-to-noise ratio is 20.8:1, with an atrazine peak of 1250 and a noise of 60. The peak area of atrazine is 5549. Bottom: Chromatogram of the internal standard deuterated atrazine.

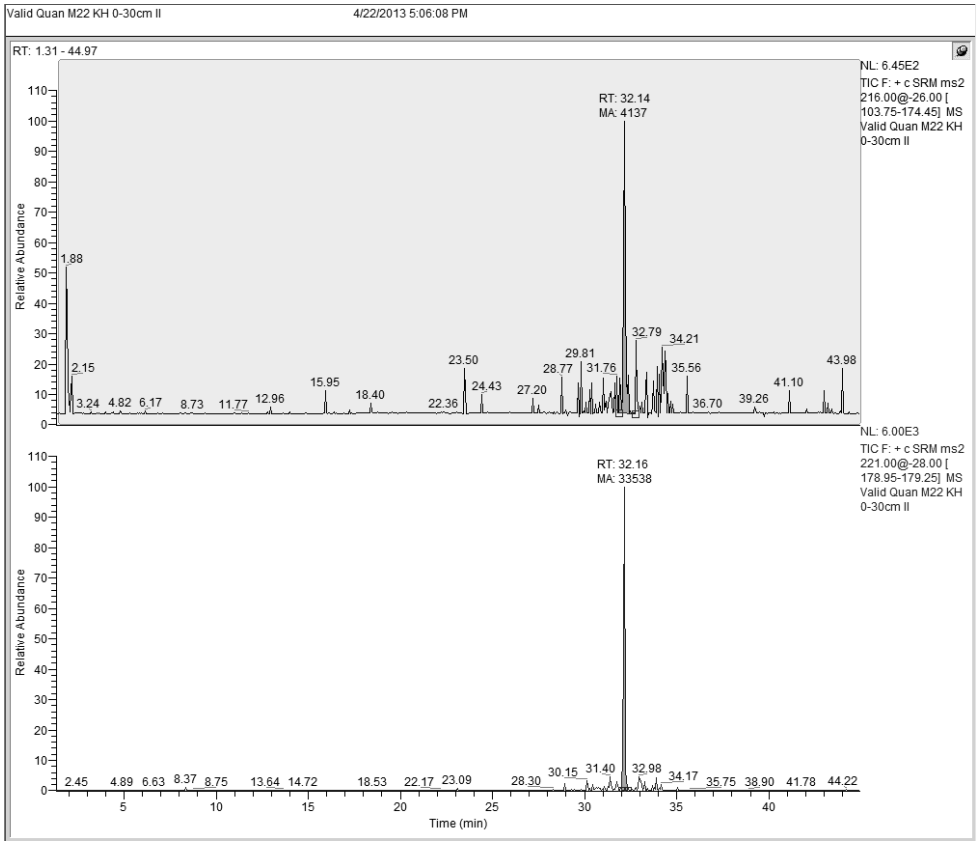

Figure 17: Top: Chromatogram of LC-MS/MS Analysis of extracts of Krauthausen Soil B (KS-B) using 135°C and 206.8 bar as ASE Parameters, with an atrazine retention time of 32.14 min. The signal-to-noise ratio is 10.8:1, with an atrazine peak of 650 and a noise of 60. The peak area of atrazine is 3920. Bottom: Chromatogram of the internal standard deuterated atrazine.

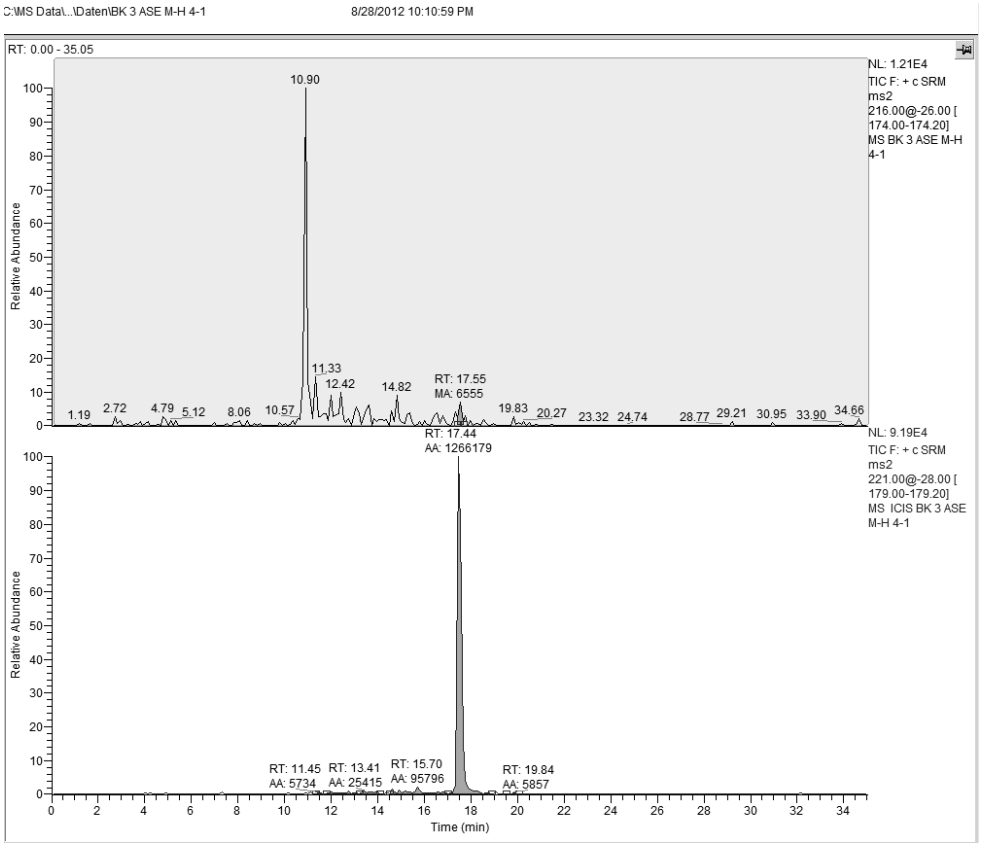

Figure 18: Top: Chromatogram of LC-MS/MS analysis of extracts of Krauthausen Soil B (KS-B) using 100°C and 206.8 bar as ASE Parameters and the old short gradient of 35 min, Atrazine is not detectable. Bottom: Chromatogram of the internal standard deuterated atrazine.

Table 18: Laboratory data of atrazine and 2-hydroxyatrazine soil residue analysis and method validation.

Krauthausen Soil B: 0-30 cm – Method validation												
Bar/Temp. [°]	Vial - Empty	Vial - Filled	$m_{Extract}$	$V_{Extract}$	2-Hydroxyatrazine		Mean Conc.	Standard deviation	Atrazine		Mean Conc.	Standard deviation
	[g]	[g]	[g]	[mL]	µg/mL	µg/kg	µg/kg	µg/kg	µg/mL	µg/kg	µg/kg	µg/kg
100/100	36.483	50.009	13.526	16.055	1.50E-04	0.241	0.233	0.010	3.47E-05	0.056	0.052	0.003
	36.869	49.364	12.495	14.831	1.49E-04	0.221			3.41E-05	0.051		
	36.752	49.869	13.117	15.569	1.51E-04	0.235			3.26E-05	0.051		
100/135	36.089	50.634	14.545	17.264	1.65E-04	0.285	0.290	0.005	4.39E-05	0.076	0.071	0.006
	36.562	51.022	14.460	17.163	1.71E-04	0.293			4.28E-05	0.073		
	35.995	50.525	14.530	17.246	1.70E-04	0.294			3.74E-05	0.064		
150/100	36.487	48.36	11.873	14.093	1.57E-04	0.221	0.249	0.025	5.43E-05	0.077	0.076	0.001
	36.108	49.78	13.672	16.228	1.60E-04	0.259			4.60E-05	0.075		
	35.784	49.614	13.830	16.415	1.63E-04	0.267			4.61E-05	0.076		
150/135	36.178	51.411	15.233	18.081	1.79E-04	0.324	0.324	0.002	3.60E-05	0.065	0.066	0.002
	36.558	51.898	15.340	18.208	1.79E-04	0.326			3.76E-05	0.068		
	36.199	51.232	15.033	17.843	1.80E-04	0.322			3.64E-05	0.065		
206.8/100	35.835	47.395	11.560	13.721	1.80E-04	0.246	0.249	0.005	9.29E-05	0.127	0.124	0.003
	36.009	47.962	11.953	14.188	1.80E-04	0.256			8.74E-05	0.124		
	36.014	47.521	11.507	13.658	1.80E-04	0.246			8.83E-05	0.121		
206.8/135	36.657	51.478	14.821	17.592	1.92E-04	0.338	0.333	0.005	4.78E-05	0.084	0.085	0.003
	36.606	51.353	14.747	17.504	1.87E-04	0.328			4.75E-05	0.083		
	36.429	51.075	14.646	17.384	1.91E-04	0.332			5.14E-05	0.089		

Soil core: Krauthausen Soil A (KS-A-1); ASE Parameters: 100°C, 206.8 bar; Extraction solvent: Methanol/Water 4:1 (v/v), ρ = 0.84 g/mL												
Sample	**Vial - Empty**	**Vial - Filled**	**$m_{Extract}$**	**$V_{Extract}$**	**2-Hydroxyatrazine**		**Mean Conc.**	**Standard deviation**	**Atrazine**		**Mean Conc.**	**Standard deviation**
	[g]	**[g]**	**[g]**	**[mL]**	**µg/mL**	**µg/kg**	**µg/kg**	**µg/kg**	**µg/mL**	**µg/kg**	**µg/kg**	**µg/kg**
0-10	36.416	46.903	10.487	12.447	1.07E-04	0.134			1.22E-04	0.151		
0-10	36.057	47.531	11.474	13.619	1.09E-04	0.148	0.138	0.009	1.24E-04	0.168	0.158	0.009
0-10	36.606	47.184	10.578	12.555	1.06E-04	0.133			1.23E-04	0.154		
10-30	37.025	50.436	13.411	15.918	8.08E-05	0.129			1.10E-04	0.175		
10-30	35.810	46.59	10.780	12.795	7.59E-05	0.097	0.113	0.016	1.11E-04	0.142	0.160	0.017
10-30	36.284	48.6	12.316	14.618	7.70E-05	0.113			1.12E-04	0.163		
30-60	36.637	49.119	12.482	14.815	5.66E-05	0.084			6.60E-05	0.098		
30-60	36.580	49.181	12.601	14.957	6.08E-05	0.091	0.088	0.004	6.59E-05	0.099	0.099	0.001
30-60	36.282	48.9	12.618	14.977	5.87E-05	0.088			6.65E-05	0.100		
60-100	36.118	48.411	12.293	14.591	3.71E-05	0.054			2.64E-05	0.039		
60-100	36.335	48.957	12.622	14.982	3.85E-05	0.058	0.056	0.002	2.61E-05	0.039	0.039	0.001
60-100	35.988	48.503	12.515	14.855	3.87E-05	0.058			2.75E-05	0.041		
100-150	36.774	49.716	12.942	15.361	2.65E-05	0.041			2.21E-05	0.034		
100-150	36.097	49.134	13.037	15.474	2.53E-05	0.039	0.040	0.001	2.25E-05	0.035	0.033	0.003
100-150	36.024	48.346	12.322	14.626	2.83E-05	0.041			2.01E-05	0.029		
150-200	35.981	48.648	12.667	15.035	3.21E-05	0.048			1.77E-05	0.027		
150-200	36.093	50.043	13.950	16.558	2.69E-05	0.044	0.053	0.012	1.59E-05	0.026	0.028	0.003
150-200	35.875	49.398	13.523	16.051	4.16E-05	0.067			1.97E-05	0.032		
200-250	36.664	50.168	13.504	16.028	2.17E-05	0.035			1.47E-05	0.024		
200-250	36.214	49.989	13.775	16.350	1.84E-05	0.030	0.032	0.003	1.34E-05	0.022	0.023	0.001
200-250	35.831	49.872	14.041	16.666	1.81E-05	0.030			1.38E-05	0.023		
250-275	36.116	49.468	13.352	15.848	1.30E-05	0.021			1.29E-05	0.020		
250-275	36.845	50.323	13.478	15.998	1.28E-05	0.020	0.018	0.004	1.15E-05	0.018	0.018	0.003
250-275	36.121	46.704	10.583	12.561	1.15E-05	0.014			1.12E-05	0.014		

Soil core: Krauthausen Soil A (KS-A-2); ASE Parameters: 100°C, 206.8 bar; Extraction solvent: Methanol/Water 4:1 (v/v), ρ = 0.84 g/mL												
Sample	Vial - Empty	Vial - Filled	$m_{Extract}$	$V_{Extract}$	2-Hydroxyatrazine		Mean Conc.	Standard deviation	Atrazine		Mean Conc.	Standard deviation
	[g]	[g]	[g]	[mL]	µg/mL	µg/kg	µg/kg	µg/kg	µg/mL	µg/kg	µg/kg	µg/kg
0-10	35.897	48.409	12.512	14.851	1.78E-04	0.265	0.248	0.016	1.47E-04	0.219	0.205	0.012
0-10	36.340	47.123	10.783	12.799	1.82E-04	0.233			1.53E-04	0.195		
0-10	36.858	48.353	11.495	13.644	1.81E-04	0.247			1.47E-04	0.201		
10-30	36.153	48.987	12.834	15.233	1.73E-04	0.264	0.250	0.013	9.75E-05	0.148	0.140	0.007
10-30	36.881	48.821	11.940	14.172	1.68E-04	0.238			9.54E-05	0.135		
10-30	36.398	48.737	12.339	14.646	1.70E-04	0.250			9.34E-05	0.137		
30-60	36.356	48.895	12.539	14.883	1.41E-04	0.210	0.205	0.009	5.10E-05	0.076	0.071	0.008
30-60	35.677	47.306	11.629	13.803	1.51E-04	0.209			5.50E-05	0.076		
30-60	36.105	47.043	10.938	12.983	1.50E-04	0.195			4.72E-05	0.061		
60-100	36.204	48.987	12.783	15.173	1.23E-04	0.186	0.182	0.005	2.54E-05	0.039	0.045	0.006
60-100	36.426	49.375	12.949	15.370	1.20E-04	0.185			3.23E-05	0.050		
60-100	36.532	49.236	12.704	15.079	1.17E-04	0.176			3.11E-05	0.047		
100-150	36.735	47.792	11.057	13.124	9.83E-05	0.129	0.133	0.006	2.22E-05	0.029	0.025	0.004
100-150	36.246	47.227	10.981	13.034	1.07E-04	0.139			1.86E-05	0.024		
100-150	36.471	46.561	10.090	11.976	1.08E-04	0.130			1.80E-05	0.022		
150-200	35.896	48.152	12.256	14.547	8.14E-05	0.118	0.124	0.006	1.79E-05	0.026	0.024	0.002
150-200	36.477	48.823	12.346	14.654	8.93E-05	0.131			1.66E-05	0.024		
150-200	36.765	48.990	12.225	14.510	8.53E-05	0.124			1.51E-05	0.022		
200-250	36.186	48.276	12.090	14.350	6.10E-05	0.088	0.083	0.004	1.34E-05	0.019	0.018	0.002
200-250	36.059	47.663	11.604	13.773	5.76E-05	0.079			1.44E-05	0.020		
200-250	36.825	48.521	11.696	13.882	5.95E-05	0.083			1.18E-05	0.016		
250-280	36.949	50.087	13.138	15.594	4.00E-05	0.062	0.061	0.001	1.09E-05	0.017	0.017	0.001
250-280	35.628	48.870	13.242	15.718	3.86E-05	0.061			1.12E-05	0.018		
250-280	36.524	48.501	11.977	14.216	4.21E-05	0.060			1.10E-05	0.016		
280-294	36.484	48.895	12.411	14.731	2.35E-05	0.035	0.032	0.005	8.25E-06	0.012	0.012	0.001
280-294	36.332	49.649	13.317	15.807	2.18E-05	0.034			7.99E-06	0.013		
280-294	35.942	49.647	13.705	16.267	1.60E-05	0.026			6.88E-06	0.011		

Soil core: Krauthausen Soil A (KS-A-3); ASE Parameters: 100°C, 206.8 bar; Extraction solvent: Methanol/Water 4:1 (v/v), ρ = 0.84 g/mL												
Sample	**Vial - Empty**	**Vial - Filled**	**$m_{Extract}$**	**$V_{Extract}$**	**2-Hydroxyatrazine**		**Mean Conc.**	**Standard deviation**	**Atrazine**		**Mean Conc.**	**Standard deviation**
	[g]	**[g]**	**[g]**	**[mL]**	**µg/mL**	**µg/kg**	**µg/kg**	**µg/kg**	**µg/ml**	**µg/kg**	**µg/kg**	**µg/kg**
0-10	36.910	48.774	11.864	14.082	1.68E-04	0.236	0.246	0.009	1.04E-04	0.146	0.147	0.004
0-10	36.702	49.434	12.732	15.112	1.68E-04	0.253			9.96E-05	0.151		
0-10	36.623	48.910	12.287	14.584	1.70E-04	0.248			9.80E-05	0.143		
10-30	35.959	48.317	12.358	14.668	1.51E-04	0.222	0.224	0.005	6.93E-05	0.102	0.097	0.007
10-30	36.793	49.173	12.380	14.694	1.50E-04	0.220			6.80E-05	0.100		
10-30	35.935	48.728	12.793	15.185	1.51E-04	0.230			5.90E-05	0.090		
30-60	36.496	48.961	12.465	14.795	8.00E-05	0.118	0.114	0.004	2.75E-05	0.041	0.038	0.002
30-60	36.784	49.178	12.394	14.711	7.60E-05	0.112			2.54E-05	0.037		
30-60	36.515	47.761	11.246	13.348	8.27E-05	0.110			2.71E-05	0.036		
60-100	36.059	47.151	11.092	13.166	6.17E-05	0.081	0.079	0.008	1.88E-05	0.025	0.023	0.003
60-100	36.079	46.171	10.092	11.979	5.87E-05	0.070			1.69E-05	0.020		
60-100	33.865	45.693	11.828	14.039	6.09E-05	0.085			1.76E-05	0.025		
100-150	36.064	49.378	13.314	15.803	4.01E-05	0.063	0.059	0.005	2.34E-05	0.037	0.034	0.004
100-150	33.966	47.034	13.068	15.511	3.87E-05	0.060			2.30E-05	0.036		
100-150	36.597	49.004	12.407	14.726	3.63E-05	0.054			2.02E-05	0.030		
150-200	33.811	45.150	11.339	13.459	2.89E-05	0.039	0.042	0.003	2.24E-05	0.030	0.025	0.005
150-200	34.096	45.793	11.697	13.884	3.16E-05	0.044			1.67E-05	0.023		
150-200	36.287	47.110	10.823	12.846	3.36E-05	0.043			1.66E-05	0.021		
200-250	34.010	45.212	11.202	13.296	3.15E-05	0.042	0.042	0.001	1.15E-05	0.015	0.017	0.002
200-250	34.106	45.913	11.807	14.014	3.11E-05	0.044			1.16E-05	0.016		
200-250	33.884	45.768	11.884	14.106	2.89E-05	0.041			1.41E-05	0.020		
250-300	33.887	47.016	13.129	15.583	2.25E-05	0.035	0.032	0.003	8.19E-06	0.013	0.012	0.001
250-300	34.055	47.259	13.204	15.672	1.95E-05	0.030			7.87E-06	0.012		
250-300	33.824	46.352	12.528	14.870	2.08E-05	0.031			7.90E-06	0.012		

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